



US009045682B2

(12) **United States Patent**  
**Tanaka et al.**(10) **Patent No.:** **US 9,045,682 B2**  
(45) **Date of Patent:** **\*Jun. 2, 2015**(54) **LIQUID CRYSTALLINE MEDIUM**(71) Applicant: **Merck Patent GmbH**, Darmstadt (DE)(72) Inventors: **Norihiko Tanaka**, Aikogun (JP);  
**Makoto Murakami**, Kanagawa Pref.  
(JP); **Shinji Nakajima**, Atsugi (JP)(73) Assignee: **Merck Patent GmbH**, Darmstadt (DE)(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.This patent is subject to a terminal dis-  
claimer.(21) Appl. No.: **13/874,733**(22) Filed: **May 1, 2013**(65) **Prior Publication Data**

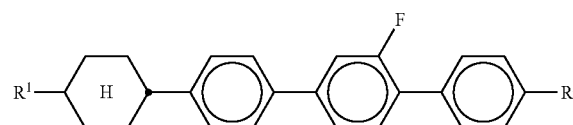
US 2013/0248761 A1 Sep. 26, 2013

**Related U.S. Application Data**(62) Division of application No. 12/601,567, filed as  
application No. PCT/EP2008/004088 on May 21,  
2008, now Pat. No. 8,454,858.(30) **Foreign Application Priority Data**

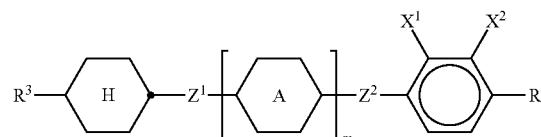
May 25, 2007 (EP) ..... 07010478

(51) **Int. Cl.****C09K 19/12** (2006.01)  
**C09K 19/34** (2006.01)  
**C09K 19/32** (2006.01)  
**C09K 19/30** (2006.01)  
**C09K 19/44** (2006.01)  
**C09K 19/04** (2006.01)(52) **U.S. Cl.**CPC ..... **C09K 19/3003** (2013.01); **C09K 19/3001**  
(2013.01); **C09K 19/44** (2013.01); **C09K**  
**2019/0407** (2013.01); **C09K 2019/3025**  
(2013.01); **C09K 19/32** (2013.01); **C09K**  
**19/3066** (2013.01); **C09K 19/3402** (2013.01);  
**C09K 19/3068** (2013.01)(58) **Field of Classification Search**CPC ..... C09K 19/3003; C09K 19/3001; C09K  
19/44; C09K 2019/0407; C09K 2019/3025;  
C09K 19/32; C09K 19/3066; C09K 19/3402;  
C09K 19/3068  
USPC ..... 252/299.61, 299.62, 299.63, 299.66  
See application file for complete search history.(56) **References Cited****U.S. PATENT DOCUMENTS**6,896,939 B2 5/2005 Klasen-Memmer et al.  
7,510,749 B2 3/2009 Shimada  
7,595,100 B2 9/2009 Fujita et al.  
7,608,310 B2 10/2009 Hattori et al.  
7,695,777 B2 4/2010 Goto et al.  
7,709,064 B2 5/2010 Torii et al.8,454,858 B2 \* 6/2013 Tanaka et al. .... 252/299.66  
8,524,117 B2 \* 9/2013 Tanaka et al. .... 252/299.6  
2006/0071195 A1 4/2006 Tomi  
2006/0198967 A1 9/2006 Saito et al.  
2007/0007493 A1 1/2007 Hattori et al.  
2007/0290169 A1 12/2007 Torii et al.  
2008/0011984 A1 1/2008 Fujita et al.  
2008/0063814 A1 3/2008 Shimada  
2008/0075891 A1 3/2008 Goto et al.  
2013/0187092 A1 \* 7/2013 Tanaka et al. .... 252/299.62  
2013/0234066 A1 \* 9/2013 Tanaka et al. .... 252/299.61**FOREIGN PATENT DOCUMENTS**EP 1 736 526 A1 12/2006  
EP 1 897 928 A1 3/2008  
EP 1 903 090 A2 3/2008  
JP 2008-88164 A 4/2008  
JP 2008-273957 A 11/2008**OTHER PUBLICATIONS**International Search Report of PCT/EP2008/004088 (Aug. 26,  
2008).K. Miyazawa et al., "First Synthesis of Liquid Crystalline 2,3-  
bis(trifluoromethyl)phenyl Derivatives Exhibiting Large Negative  
Dielectric Anisotropy" Crystals, vol. 29, No. 11 (2002) pp. 1483-  
1490.English Translation Abstract of JP 2008-088164 published Apr. 17,  
2008.English Translation Abstract of JP 2008-273957 published Nov. 13,  
2008.

\* cited by examiner

*Primary Examiner* — Geraldina Visconti(74) *Attorney, Agent, or Firm* — Millen, White, Zelano &  
Branigan, P.C.(57) **ABSTRACT**The invention relates to a liquid-crystalline medium based on  
a mixture of polar compounds having negative dielectric  
anisotropy, which contains at least one compound of the  
formula I

and at least one compound of the formula II



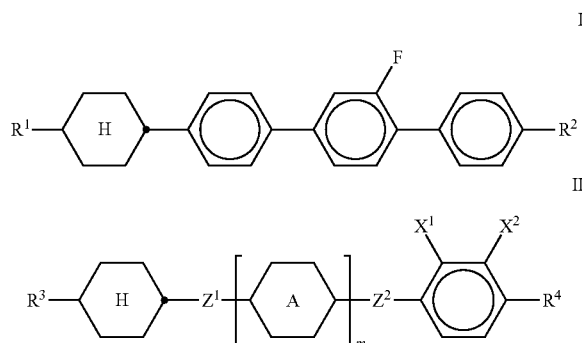
in which

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, ring A, Z<sup>1</sup>, Z<sup>2</sup> and m are as defined in Claim 1,  
and to the use thereof for an active-matrix display based on  
the ECB, VA, PS-VA, FFS, PALC or IPS effect.**24 Claims, No Drawings**

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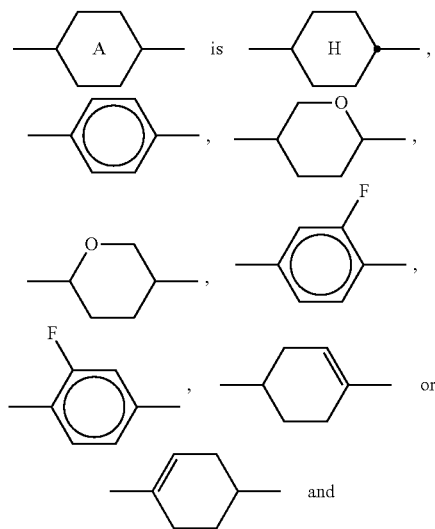
## LIQUID CRYSTALLINE MEDIUM

The invention relates to a liquid-crystalline medium based on a mixture of polar compounds having negative dielectric anisotropy, which contains at least one compound of the formula I and at least one compound of formula II



wherein

$R^1$  to  $R^4$  are each independently alkyl or alkoxy with 1 to 8 C atoms, wherein one or more  $\text{CH}_2$ -groups are optionally replaced by  $-\text{CH}=\text{CH}-$ ,  $-\text{CF}_2\text{O}-$ , or  $-\text{O}-$  in a way that  $-\text{O}-$  atoms are not linked directly to one another,



$\text{X}^1$  and  $\text{X}^2$  are each independently F, Cl or  $\text{CF}_3$ ,

$Z^1$  and  $Z^2$  are each independently a single bond,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{O}-$ ,  $-\text{OCH}_2-$ ,  $-\text{CF}_2\text{O}-$ ,  $-\text{OCF}_2-$ ,  $-\text{COO}-$

$m$  is 0 or 1.

Media of this type are to be used, in particular, for electro-optical displays with active-matrix addressing based on the ECB effect, for IPS (in plane switching) and for FFS (fringe field switching) displays.

The principle of electrically controlled birefringence, the ECB (electrically controlled birefringence) effect or DAP (deformation of aligned phases) effect was described for the first time in 1971 (M. F. Schieckel and K. Fahrenschon, "Deformation of nematic liquid crystals with vertical orientation in electrical fields", Appl. Phys. Lett. 19 (1971), 3912).

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Papers by J. F. Kahn (Appl. Phys. Lett. 20 (1972), 1193) and G. Labrunie and J. Robert (J. Appl. Phys. 44 (1973), 4869) followed.

The papers by J. Robert and F. Clerc (SID 80 Digest Techn. Papers (1980), 30), J. Duchene (Displays 7 (1986), 3) and H. Schad (SID 82 Digest Techn. Papers (1982), 244) have shown that liquid-crystalline phases must have high values for the ratio between the elastic constants  $K_3/K_1$ , high values for the optical anisotropy  $\Delta n$  and values for the dielectric anisotropy  $\Delta\epsilon$  of  $-0.5$  to  $-5$  in order to be suitable for use in high-information display elements based on the ECB effect. Electro-optical display elements based on the ECB effect have a homeotropic edge alignment. Dielectrically negative liquid-crystal media can also be used in displays which use the so-called IPS effect.

Industrial application of this effect in electro-optical display elements requires LC phases which have to satisfy a multiplicity of requirements. Particularly important here are chemical resistance to moisture, air and physical influences, such as heat, radiation in the infrared, visible and ultraviolet regions, and direct and alternating electric fields.

Furthermore, LC phases which can be used industrially are required to have a liquid-crystalline mesophase in a suitable temperature range and low viscosity.

None of the series of compounds having a liquid-crystalline mesophase that have been disclosed hitherto includes a single compound which meets all these requirements. Mixtures of two to 25, preferably three to 18, compounds are therefore generally prepared in order to obtain substances which can be used as LC phases. However, it has not been possible to prepare optimum phases easily in this manner, since no liquid-crystal materials having significantly negative dielectric anisotropy and adequate long-term stability have hitherto been available.

Matrix liquid-crystal displays (MLC displays) are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). The term "active matrix" is then used, where a distinction can be made between two types:

1. MOS (metal oxide semiconductor) transistors on a silicon wafer as substrate.
2. Thin-film transistors (TFTs) on a glass plate as substrate.

In type 1, the electro-optical effect used is usually dynamic scattering or the guest-host effect. The use of single-crystal silicon as substrate material restricts the display size, since even modular assembly of various part-displays results in problems at the joins.

In the case of the more promising type 2, which is preferred, the electro-optical effect used is usually the TN effect.

A distinction is made between two technologies: TFTs comprising compound semiconductors, such as, for example, CdSe, or TFTs based on polycrystalline or amorphous silicon. The latter technology is being worked on intensively worldwide.

The TFT matrix is applied to the inside of one glass plate of the display, while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be extended to fully colour-compatible displays, in which a mosaic of red, green and blue filters is arranged in such a way that a filter element is opposite each switchable pixel.

The TFT displays disclosed hitherto usually operate as TN cells with crossed polarisers in transmission and are back-lit.

The term MLC displays here covers any matrix display with integrated non-linear elements, i.e. besides the active

matrix, also displays with passive elements, such as varistors or diodes (MIM=metal-insulator-metal).

MLC displays of this type are particularly suitable for TV applications (for example pocket TVs) or for high-information displays in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to insufficiently high specific resistance of the liquid-crystal mixtures [TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Euro-display 84, September 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, pp. 141 ff., Paris; STROMER, M., Proc. Eurodisplay 84, September 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, pp. 145 ff., Paris]. With decreasing resistance, the contrast of an MLC display deteriorates. Since the specific resistance of the liquid-crystal mixture generally drops over the life of an MLC display owing to interaction with the inside surfaces of the display, a high (initial) resistance is very important for displays that have to have acceptable resistance values over a long operating period.

The disadvantage of the MLC-TN displays disclosed hitherto is due to their comparatively low contrast, the relatively high viewing-angle dependence and the difficulty of producing grey shades in these displays.

There thus continues to be a great demand for MLC displays having very high specific resistance at the same time as a wide operating-temperature range, short response times and low threshold voltage with the aid of which various grey shades can be produced.

The invention has the object of providing MLC displays which are based on the ECB, VA (vertical alignment), PS-VA (polymer stabilized-VA), IPS or FFS effect and do not have the disadvantages indicated above, or only do so to a lesser extent, and at the same time have very high specific resistance values.

It has now been found that this object can be achieved if nematic liquid-crystalline mixtures which contain at least one compound of the formula I and at least one compound of the formula II are used in these display elements.

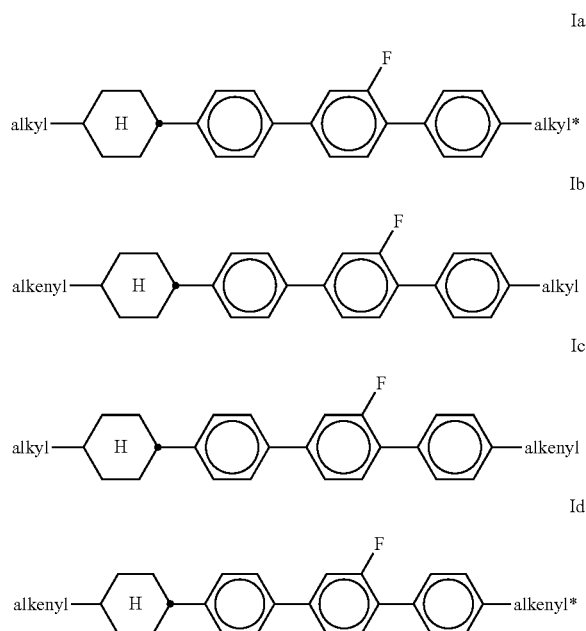
The invention thus relates to a liquid-crystalline medium having negative dielectric anisotropy which contains at least one compound of the formula I and at least one compound of the formula II.

LC compositions containing compounds of the formula I are known from U.S. 2008/0011984A1.

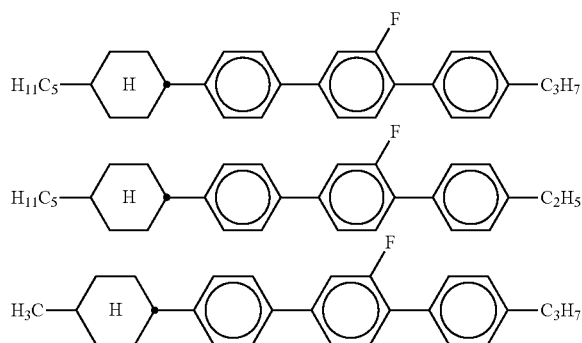
Preferred embodiments of the LC media are the following:

a)  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently of each other preferably alkyl, alkoxy or alkenyl. Alkyl and alkoxy are in each case a straight chained residue containing 1 to 6 C atoms. The term "alkenyl" comprises straight-chain and branched alkenyl groups with 2 to 7 C atoms. Straight-chain alkenyl groups are preferred. Further preferred alkenyl groups are  $C_2$ - $C_7$ -1E-alkenyl,  $C_4$ - $C_7$ -3E-alkenyl,  $C_5$ - $C_7$ -4-alkenyl,  $C_6$ - $C_7$ -5-alkenyl and  $C_7$ -6-alkenyl, in particular  $C_2$ - $C_7$ -1E-alkenyl,  $C_4$ - $C_7$ -3E-alkenyl and  $C_5$ - $C_7$ -4-alkenyl. Of these, especially preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl and 6-heptenyl. Alkenyl groups with up to 5 C atoms are particularly preferred.

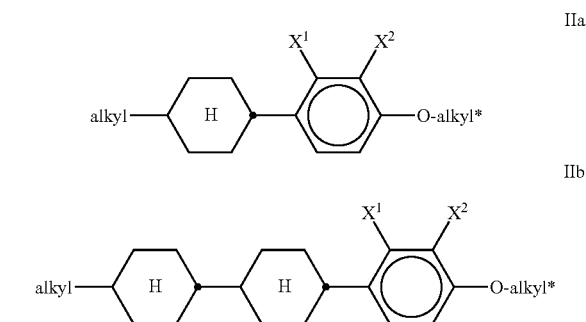
b) The compounds of formula I are selected from the following formulae,



wherein "alkyl" and "alkyl\*" independently of each other denote  $C_{1-6}$ -alkyl and "alkenyl" and "alkenyl\*" independently of each other denote  $C_{2-7}$ -alkenyl. Especially preferred are LC media containing one or more, preferably one, two or three compounds of formula Ia preferably

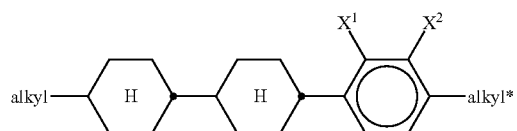


c) The compounds of formula II are selected from the following formulae IIa to IIr



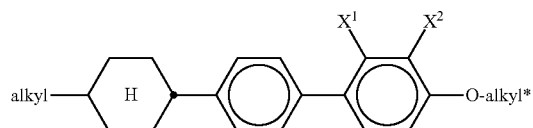
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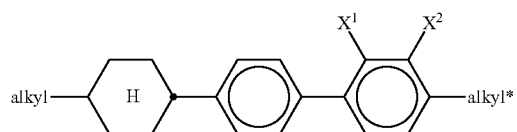
IIc

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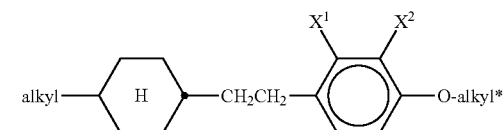
IIId

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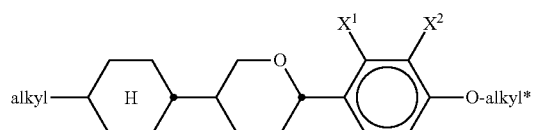
IIe

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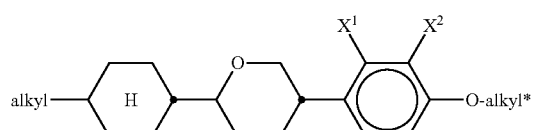
IIIf

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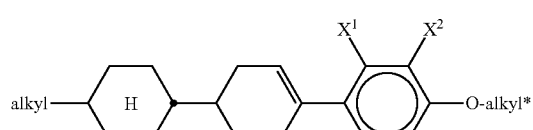
IIg

25



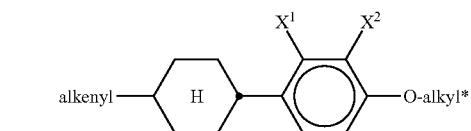
IIh

35



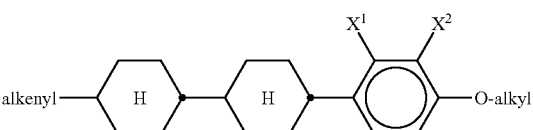
IIi

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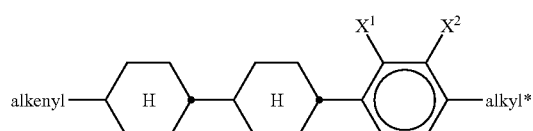
IIj

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IIk

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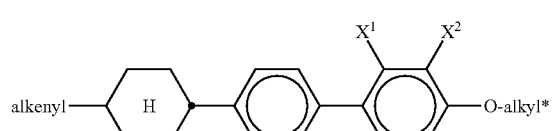


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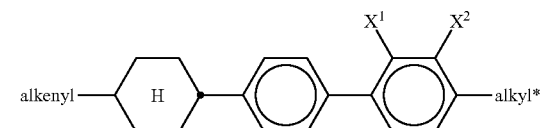
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**6**

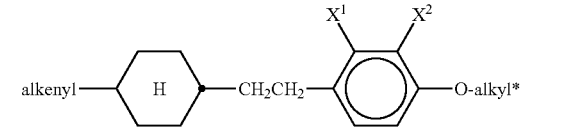
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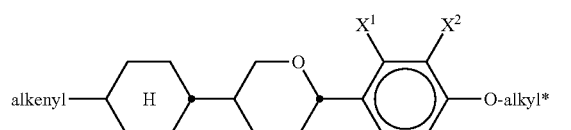
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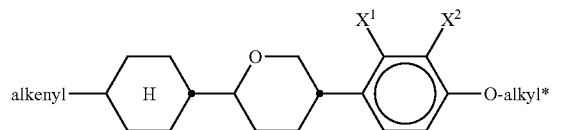
IIIn



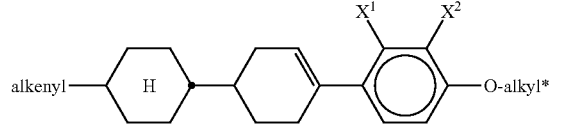
IIo



IIp



IIq

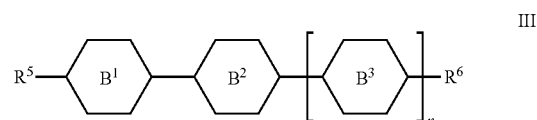


IIr

wherein "alkyl" and "alkyl\*" denote independently of each other C<sub>1-6</sub>-alkyl. "Alkenyl" denotes straight-chain alkenyl with 2 to 6 carbon atoms, preferably vinyl, CH<sub>3</sub>CH=CH, CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub> and CH<sub>3</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>. Especially preferred LC media contain at least one compound selected from the group of compounds of the formula IIa, IIb, IIc, IIe and IIi.

In the compounds of the formula II and the subformulae IIa to IIr X<sup>1</sup> and X<sup>2</sup> denote preferably F and Cl. Especially preferred are compounds wherein X<sup>1</sup>=X<sup>2</sup>=F or X<sup>1</sup>=C<sup>1</sup> and X<sup>2</sup>=F. In a preferred embodiment is X<sup>1</sup>=X<sup>2</sup>=F.

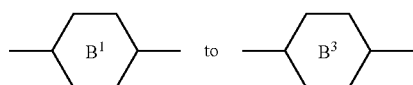
d) The LC medium additionally contains one or more compounds selected of formula III,



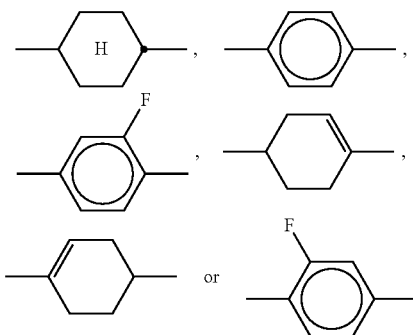
III

wherein R<sup>5</sup> and R<sup>6</sup> are independently of each other alkyl or alkoxy with 1 to 8 C atoms wherein one or more CH<sub>2</sub>-groups are optionally replaced by —CH=CH—,

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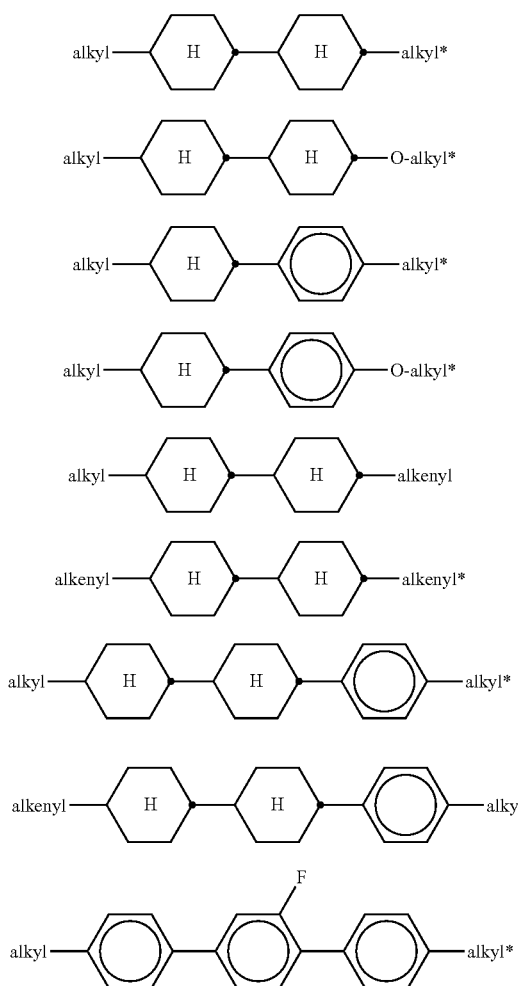


are independently of each other



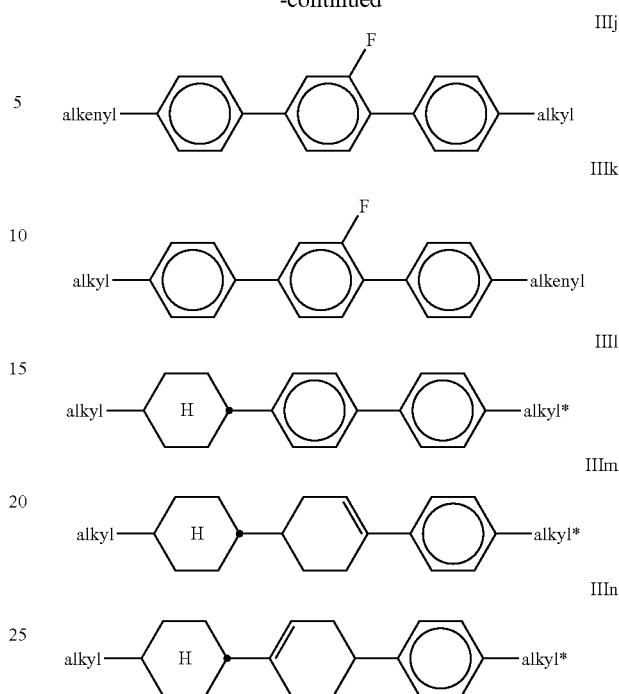
n is 0 or 1.

The compounds of formula III are selected from the sub-formulae IIIa to IIIn



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IIIa

in which  
alkyl and

IIIb

alkyl\* each, independently of one another, denote a  
straight-chain alkyl radical having 1-6 C atoms, and  
alkenyl and

IIIc

alkenyl\* each, independently of one another, denote a  
straight-chain alkenyl radical having 2-6 C atoms.

IIIe

The medium according to the invention preferably contains  
at least one compound of the formula IIIa, formula IIIb,  
formula IIIe, IIIg, IIIh, and/or IIIi. Especially preferred  
is the compound of the formula IIIi. Preferred mixtures  
contain the compound of the formula IIIi in amounts of  
5-25% by weight based on the total mixture.

IIIId

IIIe

Particularly preferred compounds of the formulae IIIe and  
IIIIf are indicated below:

IIIIf

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IIIg

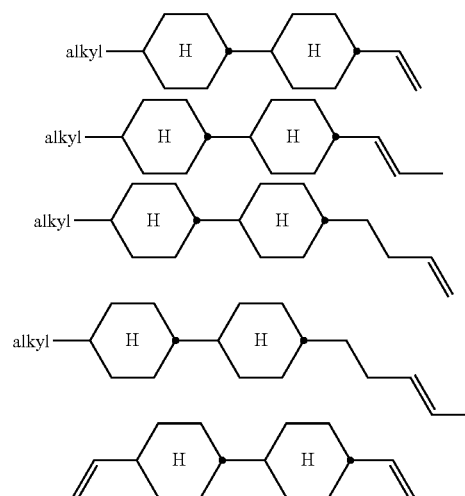
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IIIh

60

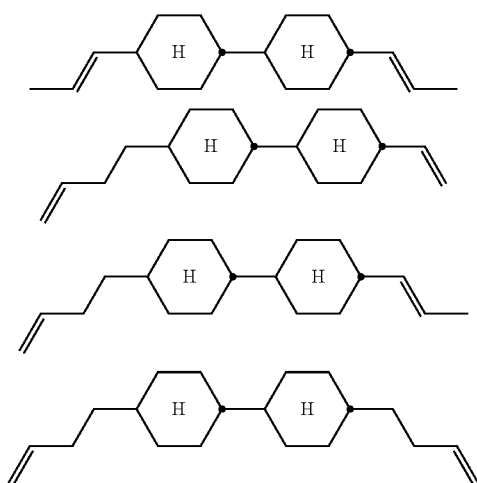
IIIi

65

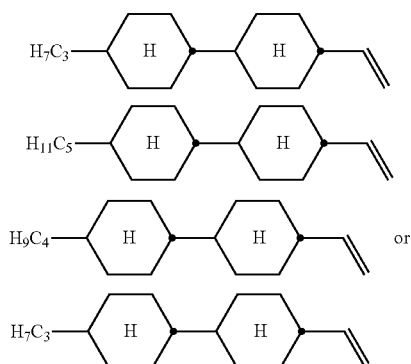


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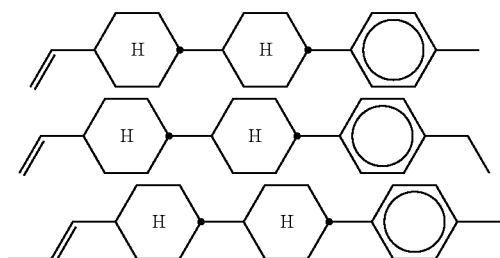
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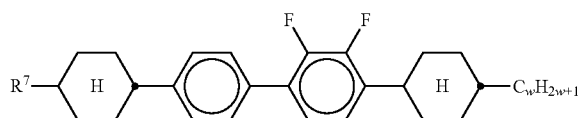
Especially preferred are LC mixtures which contain >30% by weight, most preferred  $\geq 35\%$  by weight of at least one compound of the formula



Preferred compounds of the formulae IIIh are indicated below:

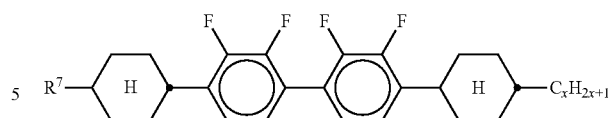


f) Liquid-crystalline medium which additionally contains one or more tetracyclic compounds of the formulae



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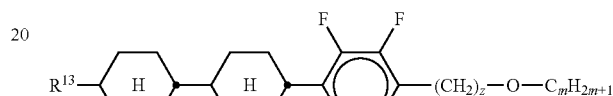
in which

$R^7$  and  $R^8$  each, independently of one another, have one of the meaning indicated for  $R^1$  in claim 1, and

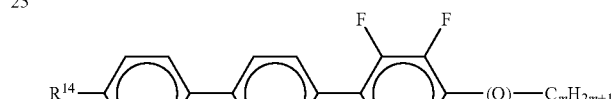
$w$  and  $x$  each, independently of one another, denote 1 to 6.

g) Liquid-crystalline medium which contains one or more compounds of the formulae Z-1 to Z-15

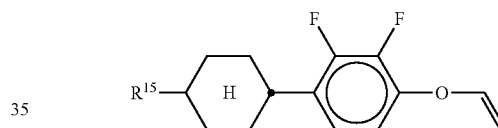
Z-1



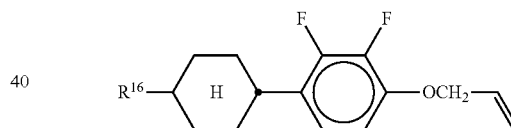
Z-2



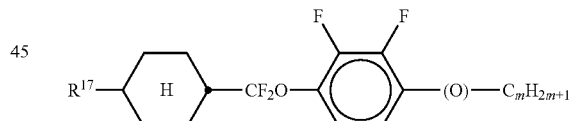
Z-3



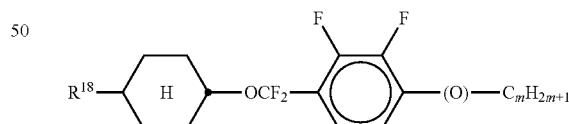
Z-4



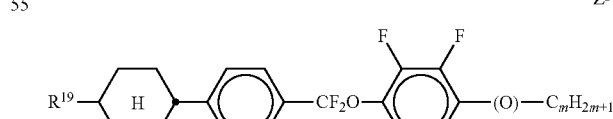
Z-5



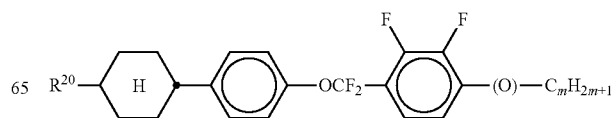
Z-6



Z-7

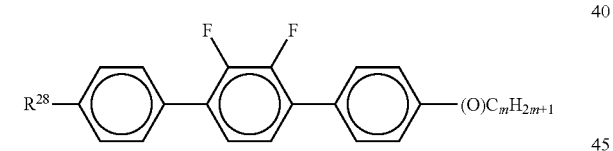
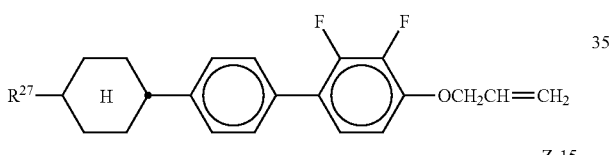
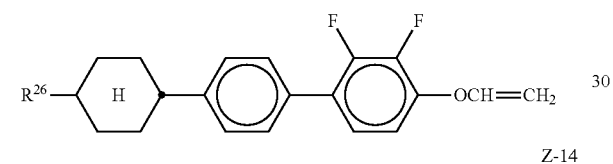
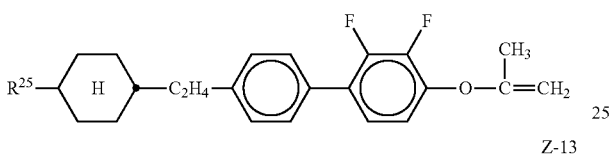
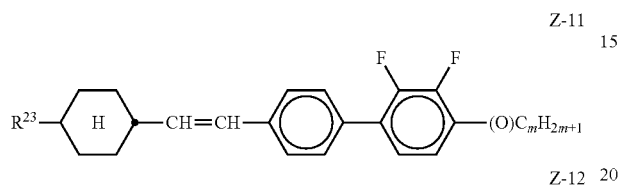
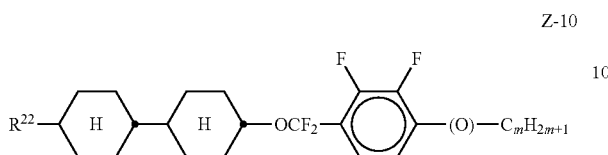
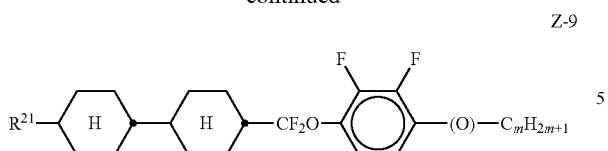


Z-8



**11**

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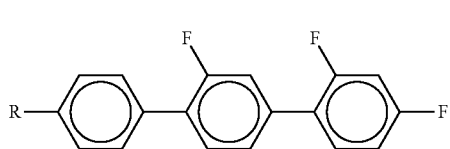


in which  $R^{13}$ - $R^{28}$  each, independently of one another, have the meanings indicated for  $R^1$ , and  $z$  and  $m$  each, independently of one another, denote 1-6.  $R^E$  denotes H,  $CH_3$ ,  $C_2H_5$  or  $n-C_3H_7$ .

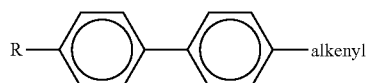
Especially preferred is the compound of the formula Z-15.

Preferred LC mixtures contain 5-25% by weight of the compound of the formula Z-15 based on the total mixture.

h) Liquid-crystalline medium which additionally contains one or more biphenyl or terphenyl compounds of the formulae T-1 and B-1

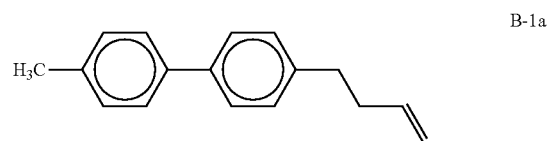
**12**

-continued



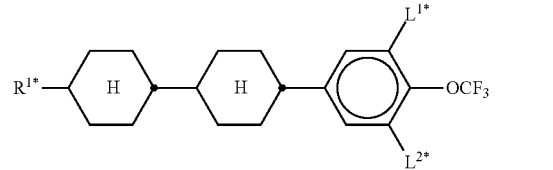
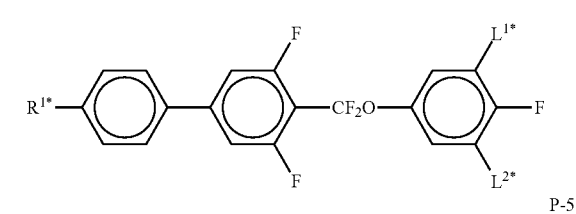
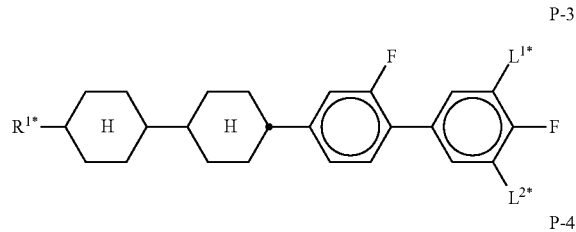
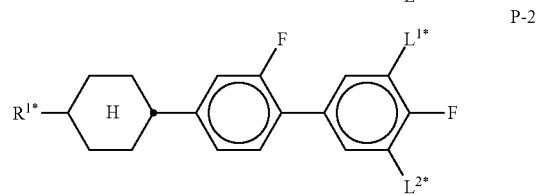
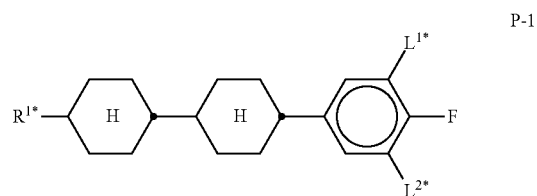
in which R denotes alkyl, alkenyl, alkoxy, alkylalkoxy or alkenyloxy having 1 or 2 to 6 C atoms, and alkenyl has the meaning indicated above.

A preferred compound of the formula B-1 is a compound of the formula B-1a



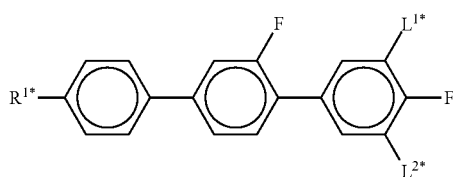
LC mixtures containing 5-25% by weight of at least one compound of the formula T-1 and/or B-1 are preferred.

i) Liquid-crystalline medium which contains at least one compound with a positive delta epsilon ( $\Delta\epsilon$ ) selected from the formulae P-1 to P-6,



**13**

-continued



P-6

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in which R<sup>1\*</sup> has the meaning of R<sup>1</sup> in claim 1 and in L<sup>1\*</sup> and L<sup>2\*</sup> each independently of one another denote H or F.

Particularly preferred media contain one or more compounds selected from the compounds of the formulae P-1 to P-6 wherein L<sup>1\*</sup> and L<sup>2\*</sup> are both F.

Preferred mixtures according to the present invention contain ≤10% by weight of the compounds of the formulae P-1 to P-6.

j) Particularly preferred media contain one or more compounds of the formula II wherein X<sup>1</sup>=X<sup>2</sup>=F.

k) Liquid-crystalline medium in which the proportion of the compounds of the formula III in the mixture as a whole is from 0 to 50% by weight preferably from 3 to 50% by weight.

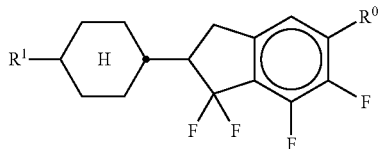
l) Liquid-crystalline medium which contains at least one indane compound selected from the formulae In-1 to In-18:

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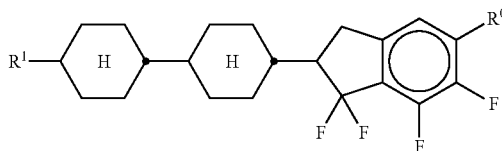
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In-1



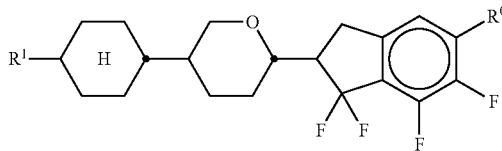
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In-2



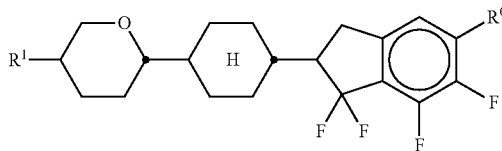
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In-3



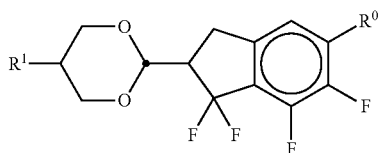
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In-4



55

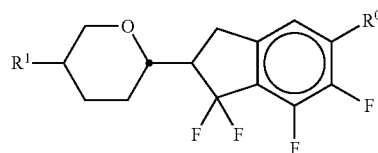
In-5



65

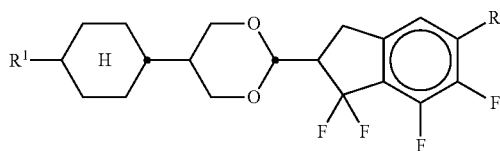
**14**

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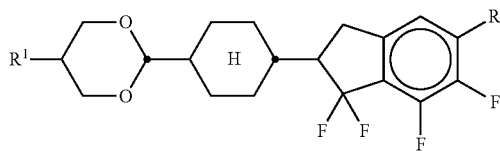


In-6

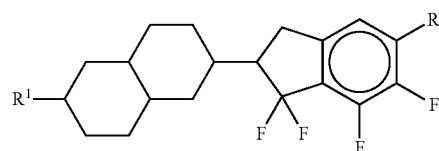
In-7



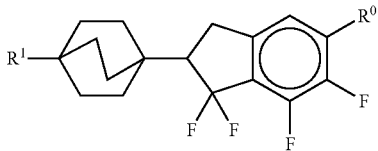
In-8



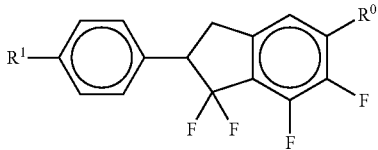
In-9



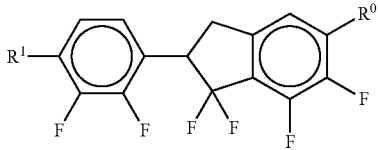
In-10



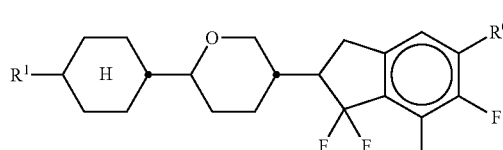
In-11



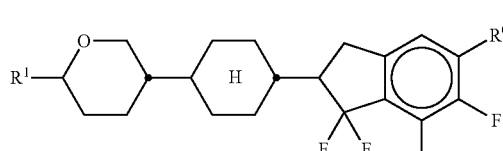
In-12



In-13



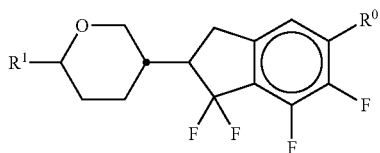
In-14



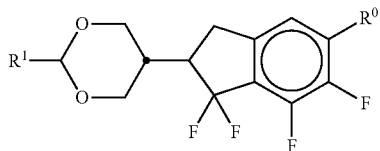


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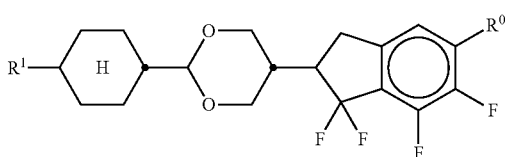
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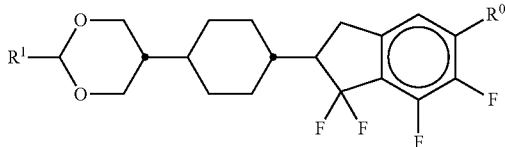
In-15



In-16



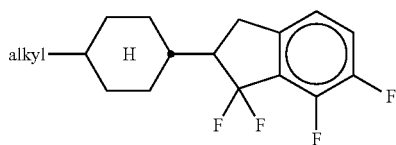
In-17



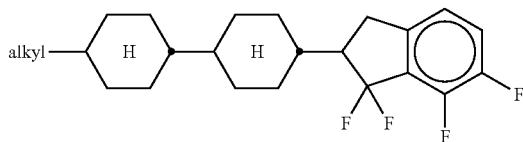
In-18

Preferred LC mixtures contain at least 5-20% by weight of at least one compound of the formula In-1 to In-18.

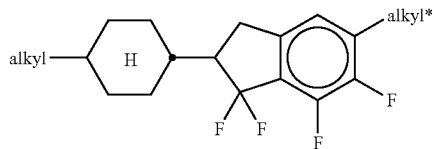
Particularly preferred media contain one or more compounds selected from the group consisting of the compounds of the formulae:



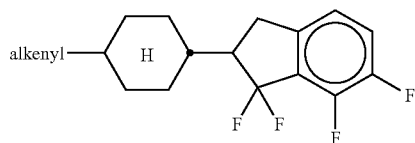
In-1a



In-2a



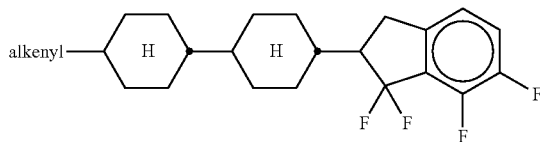
In-1b



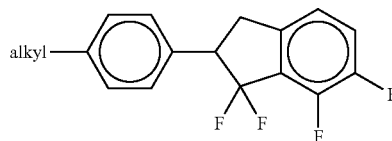
In-1c

**16**

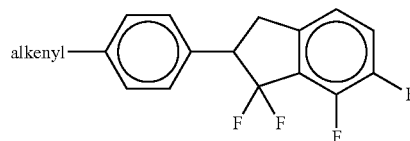
-continued



In-2b



In-11a



In-11b

Particular preference is given to media which contain at least one compound of the formula In-1a.

m) Liquid-crystalline medium which contains one, two, three, four or more, preferably at least two compounds of the formula II.

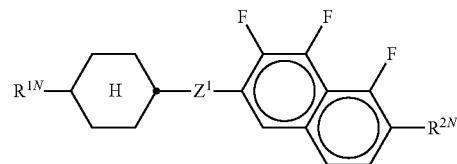
n) Liquid-crystalline medium in which R¹ and R² in the formula I preferably have independently of each other the following meanings: straight-chain alkyl, vinyl, 1E-alkenyl or 3-alkenyl.

If R¹ denotes alkenyl, it is preferably CH₂=CH, CH₃—CH=CH, C₃H₇—CH=CH, CH₂=CH—C₂H₄ or CH₃—CH=CH—C₂H₄.

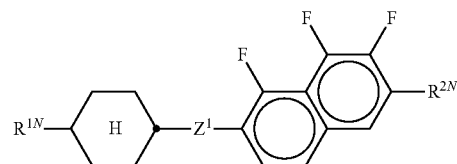
o) Liquid-crystalline medium in which the proportion of compounds of the formula I in the mixture as a whole is 1 to 30% by weight, preferably at least 5% by weight, most preferably 5 to 15% by weight, based on the total mixture.

p) Liquid-crystalline medium in which the proportion of compounds of the formula II in the mixture as a whole is at least 30% by weight, preferably at least 40%.

q) Preferred liquid-crystalline media according to the invention contain one or more substances with a tetrahydronaphthyl or naphthyl unit, such as, for example, the compounds of the formulae N-1 to N-5.



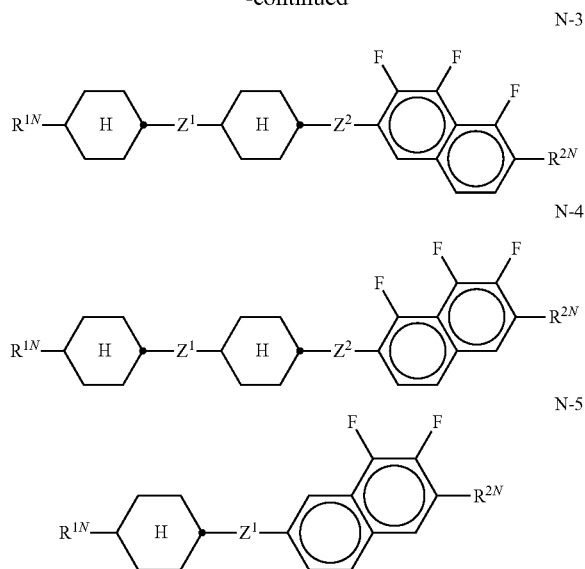
N-1



N-2

17

-continued



in which  $R^{1N}$  and  $R^{2N}$  each, independently of one another, have the meaning of  $R^1$  in claim 1.

r) Preferred mixture concepts are given in the following.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula II and
- at least one compound of the formula T-1.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula II, and
- at least one compound of the formula B-1.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula II, and
- at least one compound of the formula Z-15.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula II, and
- at least one compound of the formula In-1 to In-18.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula IIj, IIk and/or III.

LC mixture contains

- at least one compound of the formula I, preferably at least one compound of the formula Ia, and
- at least one compound of the formula IIr.

LC mixture contains at least one compound of the formula with the acronym CCOC-n-m listed in the following table.

LC mixture contains at least one compound of the formula with the acronym CCPC-n-mr listed in the following table.

LC mixture contains at least one compound of the formula with the acronym CH-nmr listed in the following table.

The invention furthermore relates to an electro-optical display with active-matrix addressing based on the ECB effect, characterised in that it contains, as dielectric, a liquid-crystalline medium according to one of Claims 1 to 9.

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The liquid-crystalline medium preferably has a nematic phase range of at least 60 K and a flow viscosity  $\eta_{20}$  of at most  $30 \text{ mm}^2 \cdot \text{s}^{-1}$  at  $20^\circ \text{C}$ .

The liquid-crystalline mixture according to the invention has a  $\Delta\epsilon$  of about  $-0.5$  to  $-8.0$ , in particular about  $-3.0$  to  $-6.0$ , where  $\Delta\epsilon$  denotes the dielectric anisotropy. The rotational viscosity  $\gamma_1$  is preferably  $<150 \text{ mPa} \cdot \text{s}$ , in particular  $<140 \text{ mPa} \cdot \text{s}$ .

The birefringence  $\Delta n$  in the liquid-crystal mixture is generally from  $0.07$  to  $0.18$ , preferably from  $0.08$  to  $0.16$ , most preferably from  $0.08$  to  $0.13$ .

The mixtures according to the invention are suitable for all VA-TFT applications, such as, for example, MVA, PVA, ASV and PS-VA. They are furthermore suitable for IPS, FFS and PALC applications with negative  $\Delta\epsilon$ .

The individual components of the formulae I, II and III of the liquid-crystal phases according to the invention are either known or their methods of preparation can easily be derived from the prior art by the person skilled in the relevant art since they are based on standard methods described in the literature.

The nematic liquid-crystal mixtures in the displays according to the invention generally comprise two components A and B, which themselves consist of one or more individual compounds.

Component A has significantly negative dielectric anisotropy and gives the nematic phase a dielectric anisotropy of  $\leq -0.3$ . It preferably comprises compounds of the formulae II.

The proportion of component A is preferably between  $30$  and  $99\%$ , in particular between  $40$  and  $90\%$ .

For component A, one (or more) individual compound(s) which has (have) a value of  $\Delta\epsilon$  of  $\leq -0.8$  is (are) preferably selected. This value must be more negative the smaller the proportion A in the mixture as a whole.

Component B has pronounced nematogenicity and a flow viscosity of not greater than  $30 \text{ mm}^2 \cdot \text{s}^{-1}$ , preferably not greater than  $25 \text{ mm}^2 \cdot \text{s}^{-1}$ , at  $20^\circ \text{C}$ .

Particularly preferred individual compounds in component B are extremely low-viscosity nematic liquid crystals having a flow viscosity of not greater than  $18 \text{ mm}^2 \cdot \text{s}^{-1}$ , preferably not greater than  $12 \text{ mm}^2 \cdot \text{s}^{-1}$ , at  $20^\circ \text{C}$ .

Component B is monotropically or enantiotropically nematic, has no smectic phases and is able to prevent the occurrence of smectic phases down to very low temperatures in liquid-crystal mixtures. For example, if various materials of high nematogenicity are added to a smectic liquid-crystal mixture, the nematogenicity of these materials can be compared through the degree of suppression of smectic phases that is achieved.

A multiplicity of suitable materials is known to the person skilled in the art from the literature. Particular preference is given to compounds of the formulae I, II and III.

In addition, these liquid-crystal phases may also comprise more than  $18$  components, preferably  $18$  to  $25$  components.

The phases preferably comprise  $4$  to  $15$ , in particular  $5$  to  $12$ , compounds of the formulae I, II and optionally III.

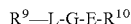
Besides compounds of the formulae I, II and III, other constituents may also be present, for example in an amount of up to  $45\%$  of the mixture as a whole, but preferably up to  $35\%$ , in particular up to  $10\%$ .

The other constituents are preferably selected from nematic or nematogenic substances, in particular known substances, from the classes of the azoxybenzenes, benzyldiene-anilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexylbiphe-

## 19

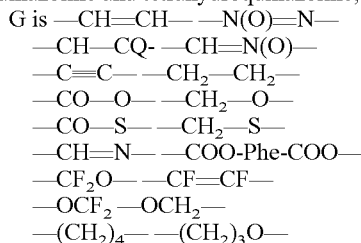
nyls or cyclohexyl-pyrimidines, phenyl- or cyclohexyldioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acids.

The most important compounds which are suitable as constituents of liquid-crystal phases of this type can be characterised by the formula IV



IV

in which L and E each denote a carbocyclic or heterocyclic ring system from the group formed by 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,



or a C—C single bond, Q denotes halogen, preferably chlorine, or —CN, and  $R^9$  and  $R^{10}$  each denote alkyl, alkenyl,

## 20

alkoxy, alkanoyloxy or alkoxycarbonyloxy having up to 18, preferably up to 8 carbon atoms, or one of these radicals alternatively denotes CN, NC, NO<sub>2</sub>, NCS, CF<sub>3</sub>, OCF<sub>3</sub>, F, Cl or Br.

In most of these compounds,  $R^9$  and  $R^{10}$  are different from one another, one of these radicals usually being an alkyl or alkoxy group. Other variants of the proposed substituents are common. Many such substances or also mixtures thereof are also commercially available. All these substances can be prepared by methods known from the literature.

It goes without saying for the person skilled in the art that the VA, IPS or PALC mixture according to the invention may also comprise compounds in which, for example, H, N, O, Cl and F have been replaced by the corresponding isotopes.

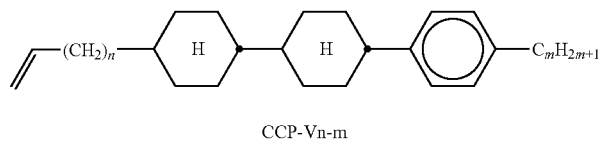
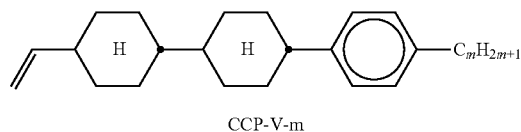
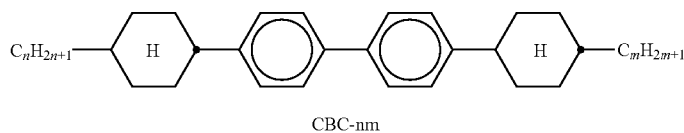
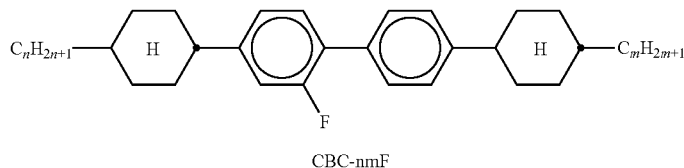
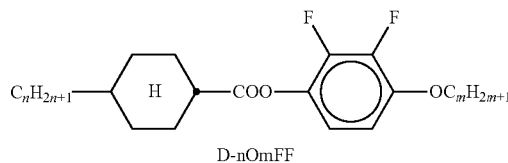
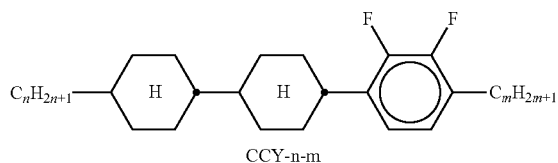
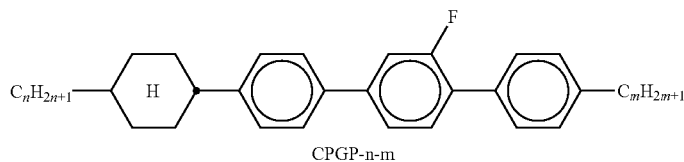
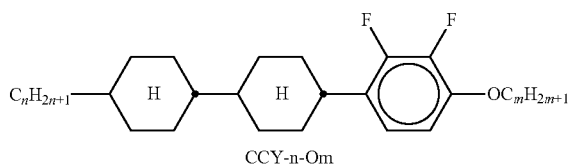
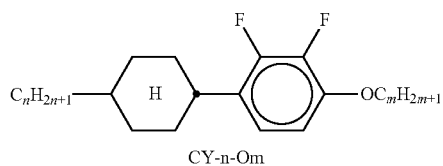
The construction of the liquid-crystal displays according to the invention corresponds to the usual geometry, as described, for example, in EP-A 0 240 379.

The following examples are intended to explain the invention without limiting it. Above and below, percentages are percent by weight based on the total mixture; all temperatures are indicated in degrees Celsius.

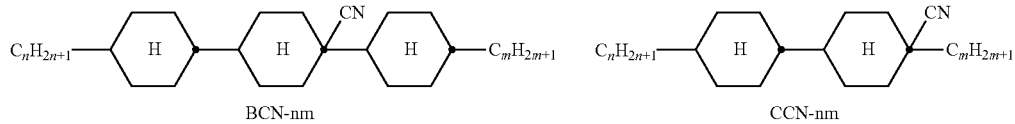
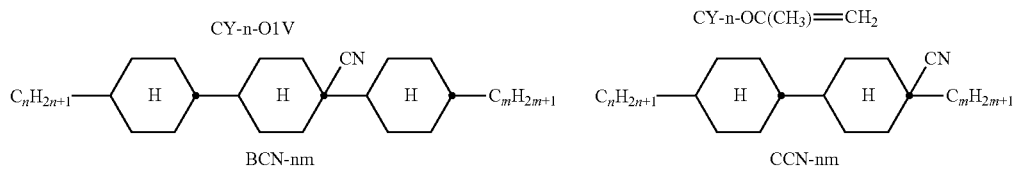
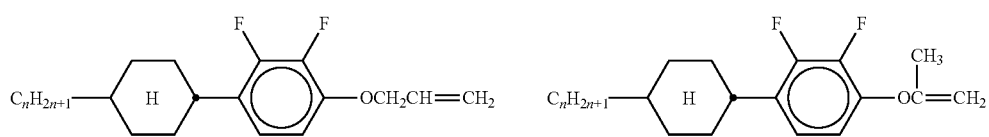
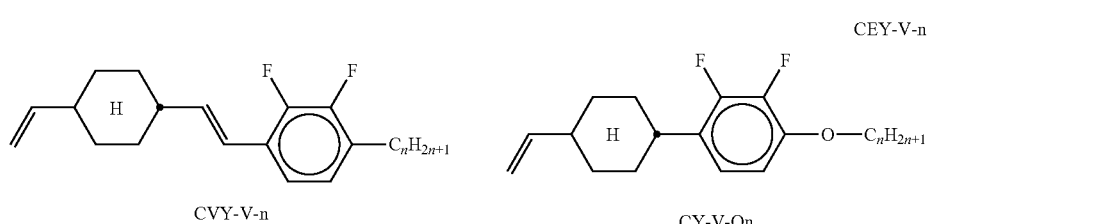
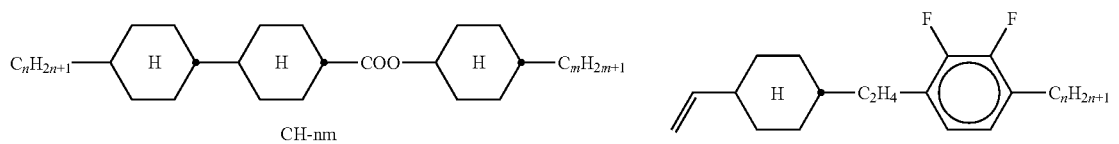
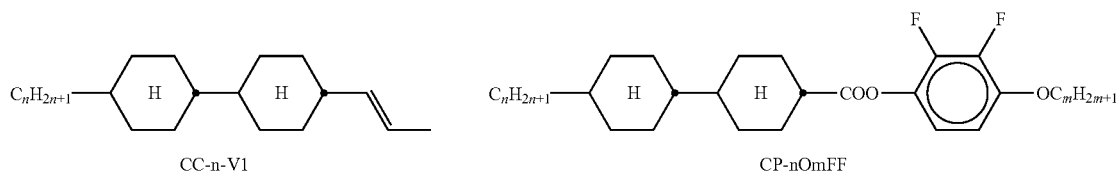
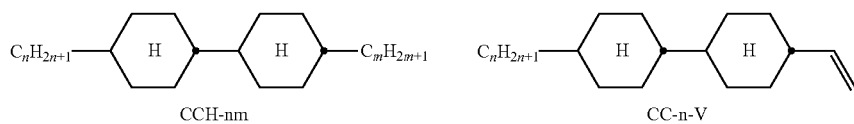
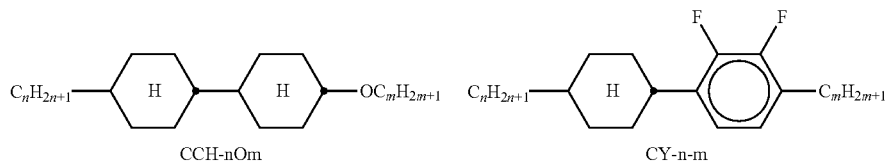
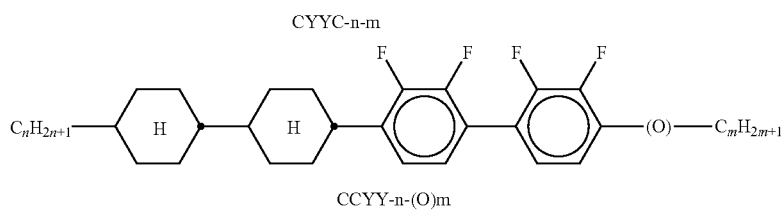
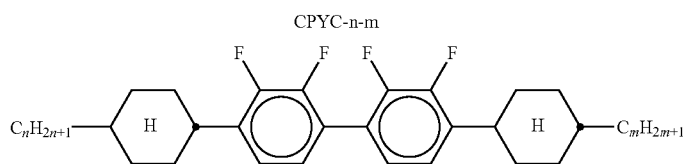
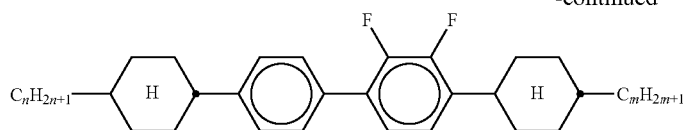
Besides the compounds of the formulae I and II, the mixtures according to the invention preferably comprise one or more of the compounds shown below.

The following abbreviations are used:

(n and m=1-6; z=1-6; m(O)m denotes n-m or n-Om)



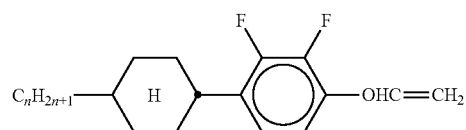
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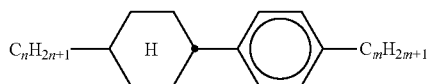
23

24

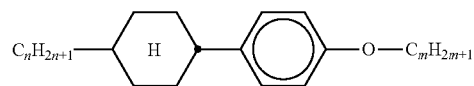
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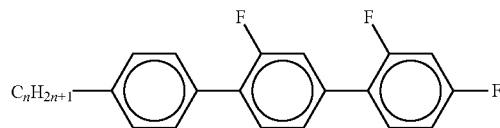
CY-n-OV



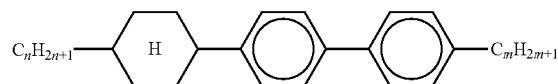
PCH-nm



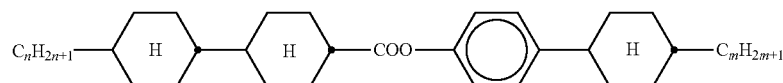
PCH-nOm



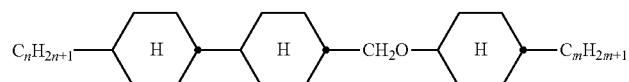
PGIGI-n-F



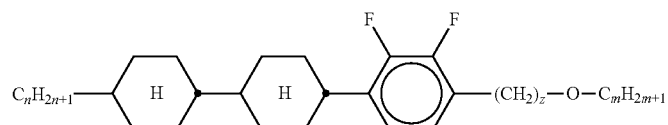
BCH-nm



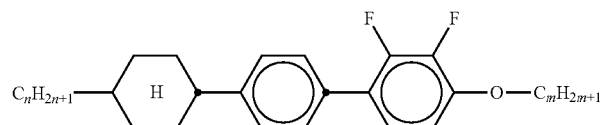
CCPC-n-m



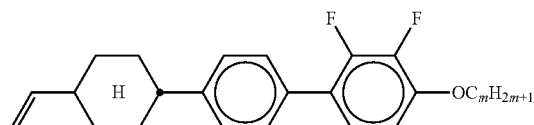
CCOC-n-m



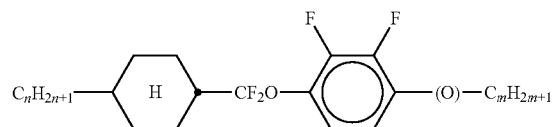
CCY-n-zOm



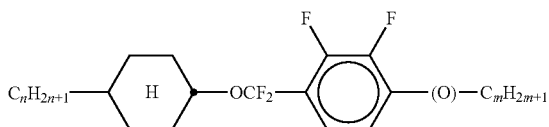
CPY-n-Om



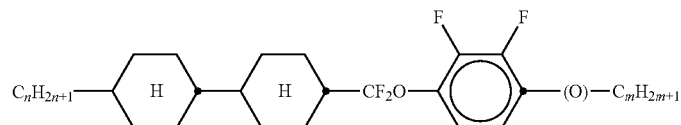
CPY-V-Om



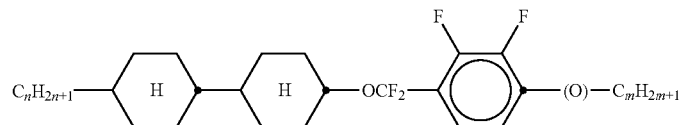
CQY-n-(O)m



CQIY-n-(O)m



CCQY-n-(O)m

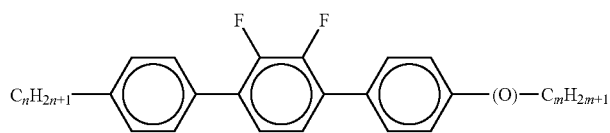


CCQIY-n-(O)m

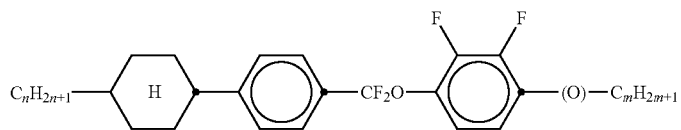
25

26

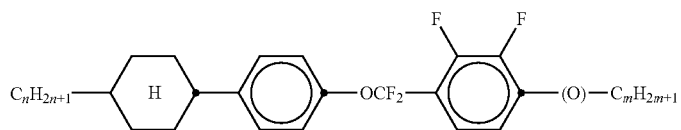
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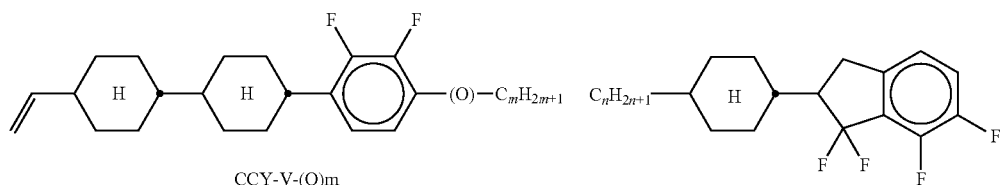
PYP-n-(O)m



CPQY-n-(O)m

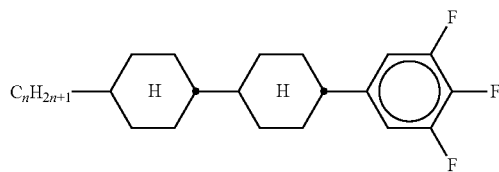


CPQIY-n-(O)m

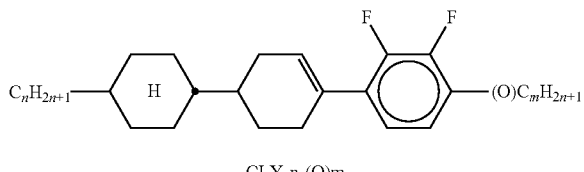


CCY-V-(O)m

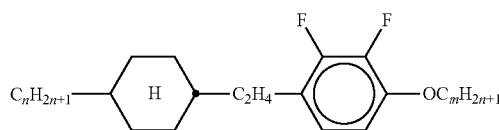
CK-n-F



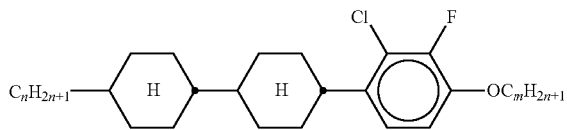
CCP-nF.F.F



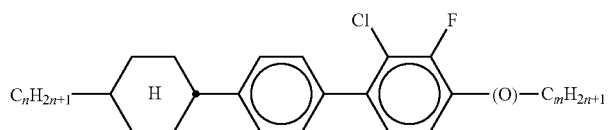
CLY-n-(O)m



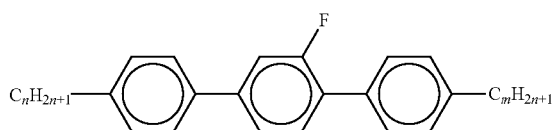
CEY-n-Om



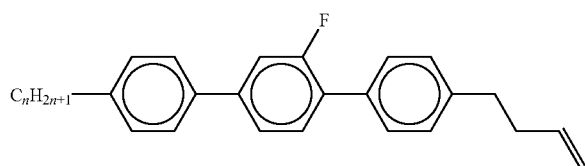
CCY(Cl,F)-n-Om



CPY(Cl,F)-n-(O)m



PGP-n-m



PGP-n-2V

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The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner which is conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after mixing.

The dielectrics may also comprise further additives known to the person skilled in the art and described in the literature, such as, for example, UV absorbers, nanoparticles, nanobeads, microparticles, antioxidants and free-radical scavengers. For example, 0-15% of pleochroic dyes, stabilisers or chiral dopants may be added.

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For example, 0-15% of pleochroic dyes may be added, furthermore conductive salts, preferably ethyldimethyldodecylammonium 4-hexoxybenzoate, tetrabutylammonium tetraphenylboranate or complex salts of crown ethers (cf., for example, Haller et al., Mol. Cryst. Liq. Cryst. Volume 24, pages 249-258 (1973)) in order to improve the conductivity or substances may be added in order to modify the dielectric anisotropy, the viscosity and/or the alignment of the nematic phases. Substances of this type are described, for example, in DE-A 22 09 127, 22 40 864, 23 21 632, 23 38 281, 24 50 088, 26 37 430 and 28 53 728.

Table A shows for example possible dopants which can be added to the mixtures according to the invention. If the mixtures according to the invention comprise a dopant, it is generally added in amounts of 0.01 to 4.0% by weight, preferably 0.1 to 1.0% by weight.

TABLE A

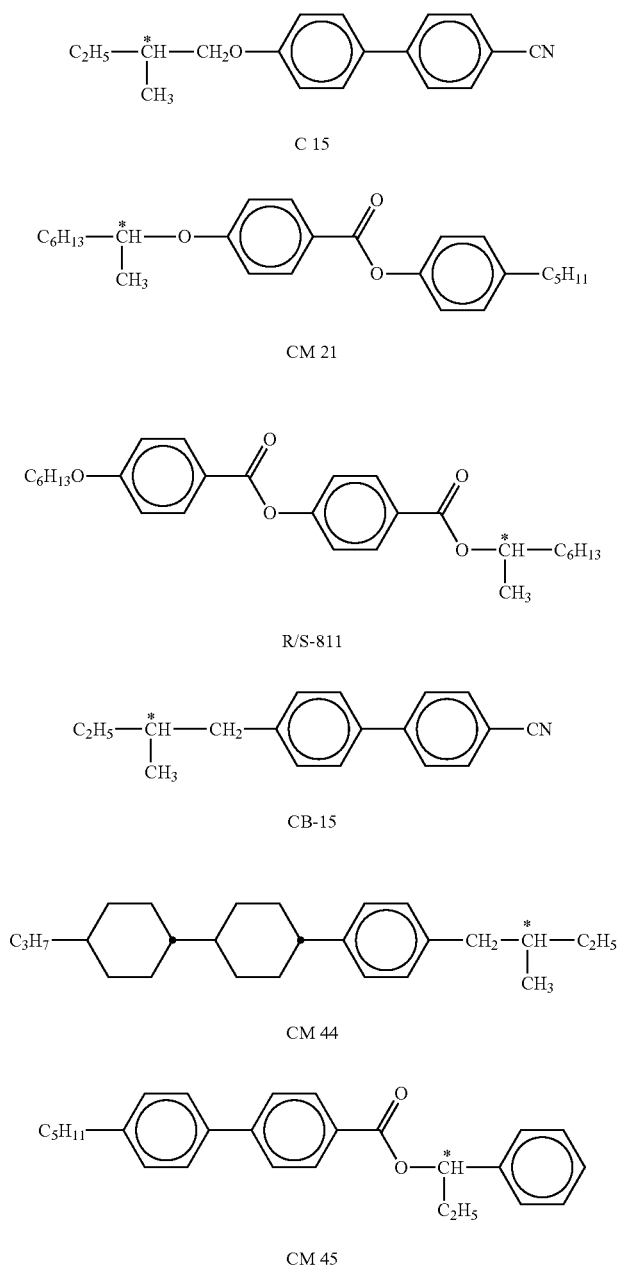


TABLE A-continued

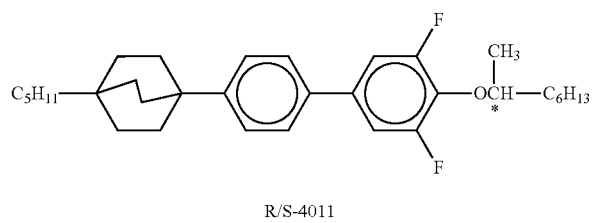
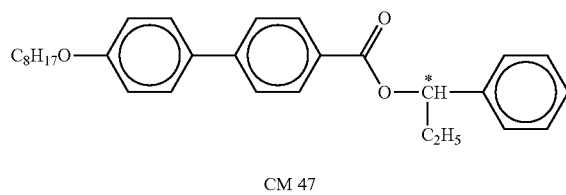
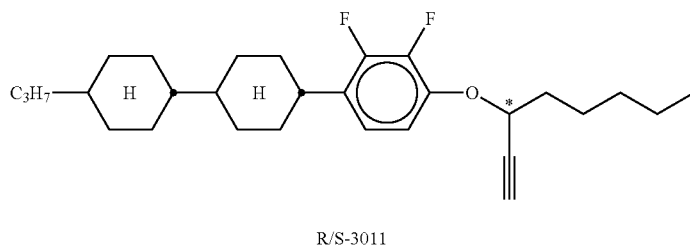
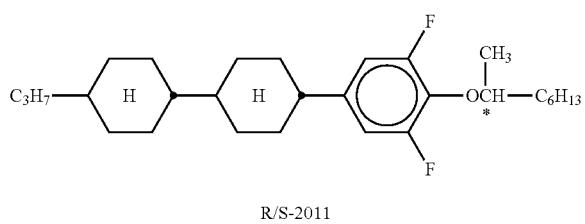
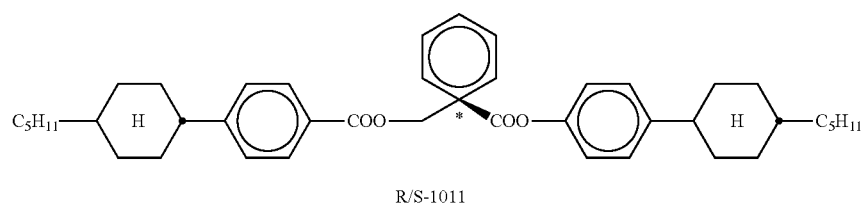
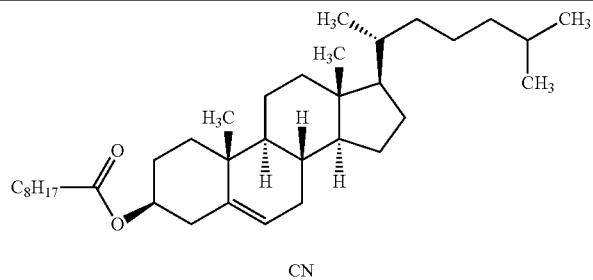
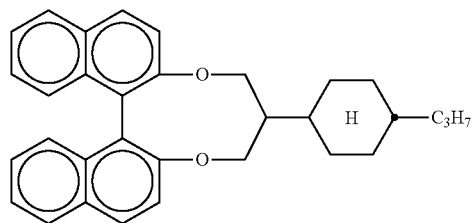




TABLE A-continued

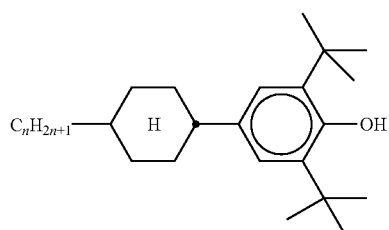
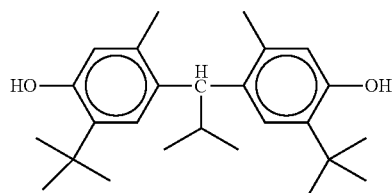
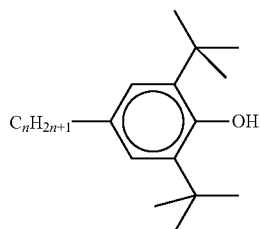
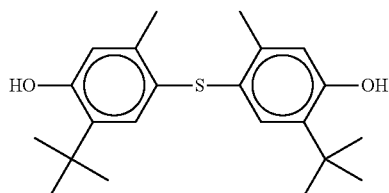
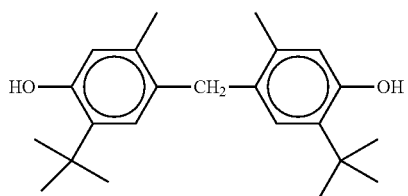


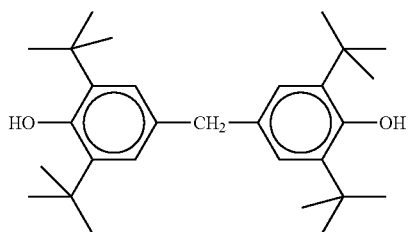
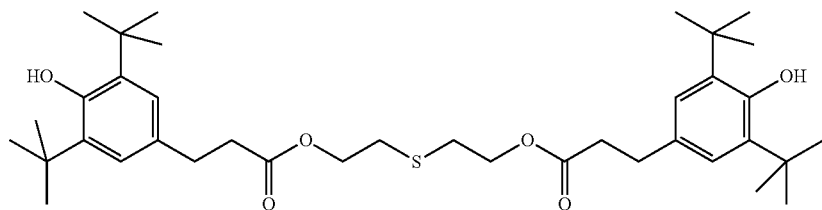
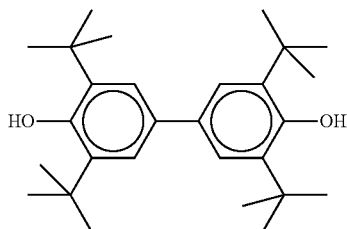
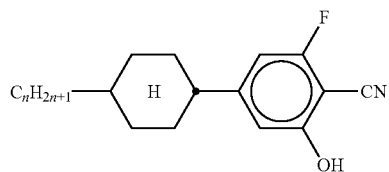
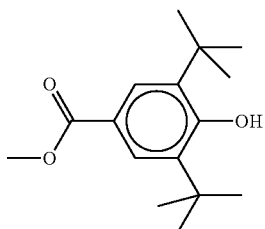
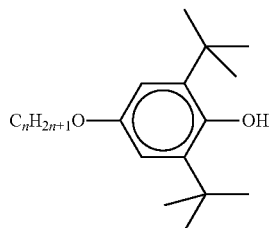
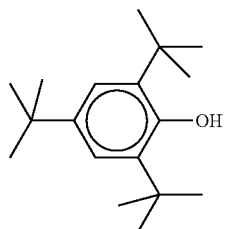
R/S-5011

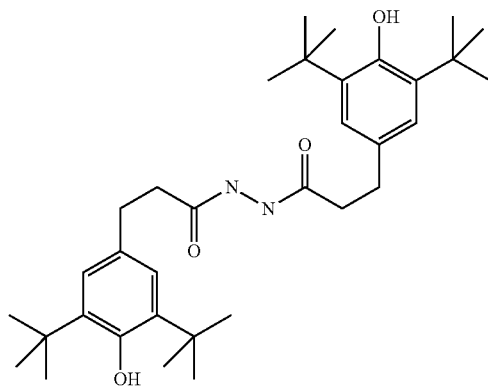
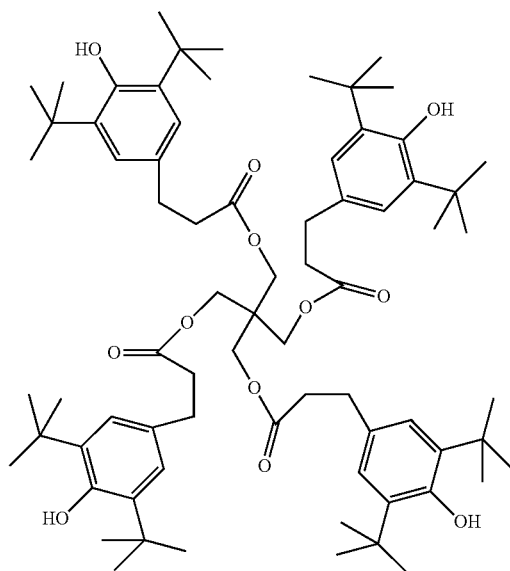
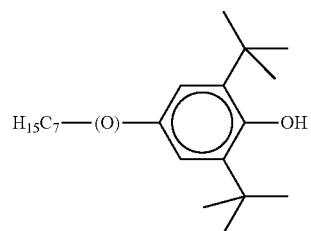
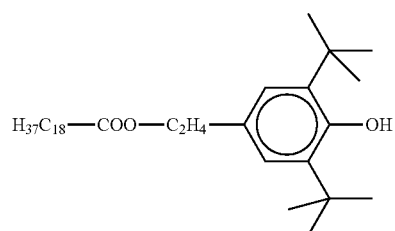
Stabilisers which can be added, for example, to the mix-<sup>15</sup>  
tures according to the invention are shown below in Table B.

TABLE B

( n = 1-12)







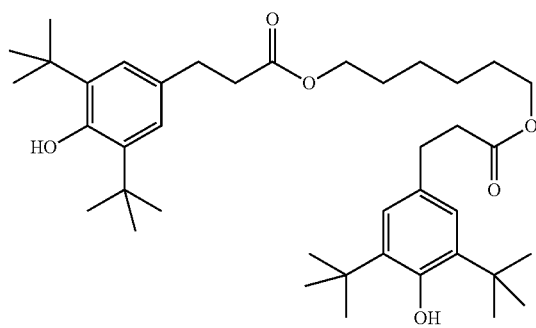
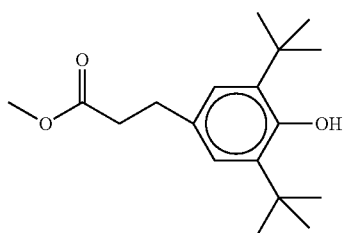
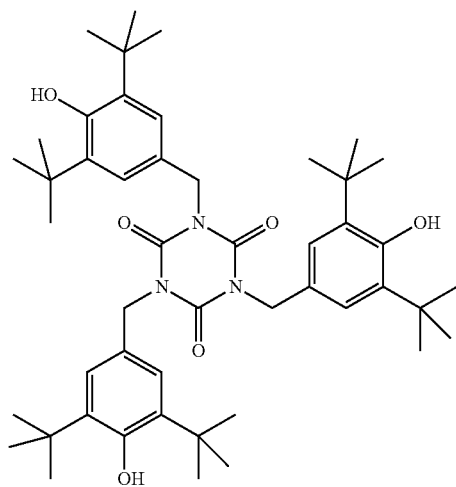
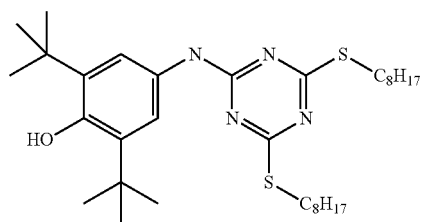
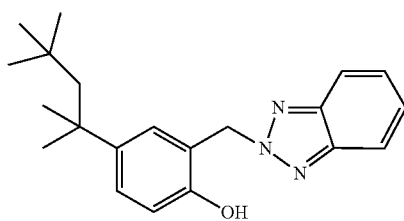
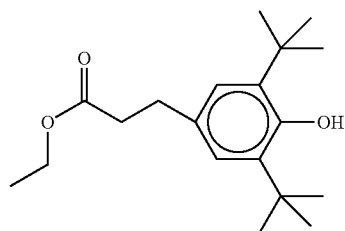
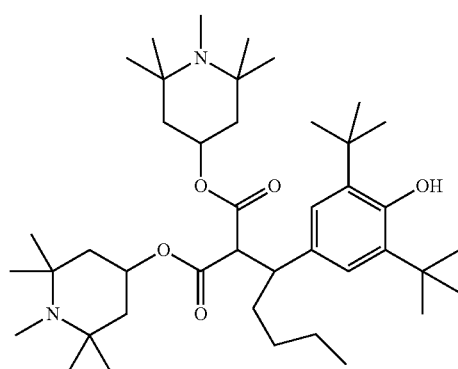
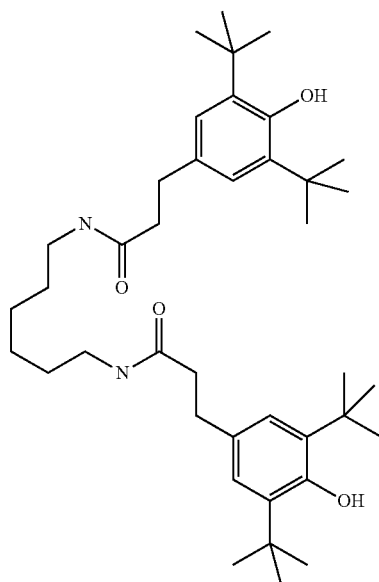


TABLE B-continued



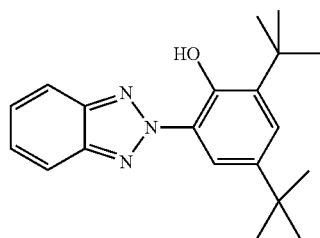
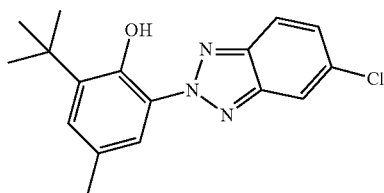
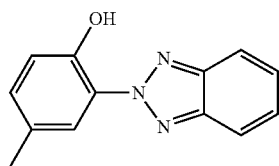
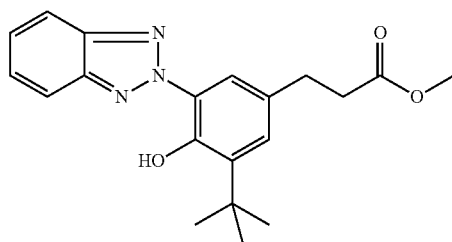
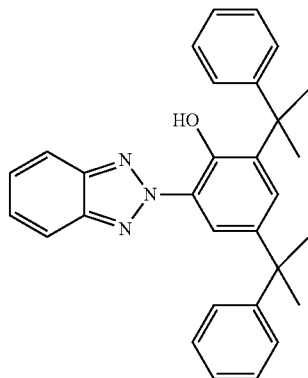
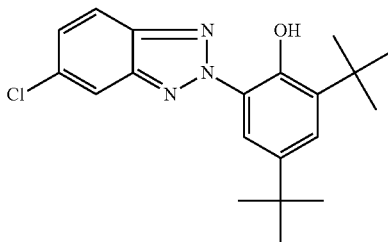
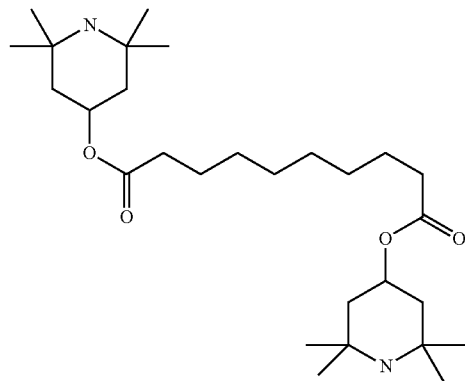
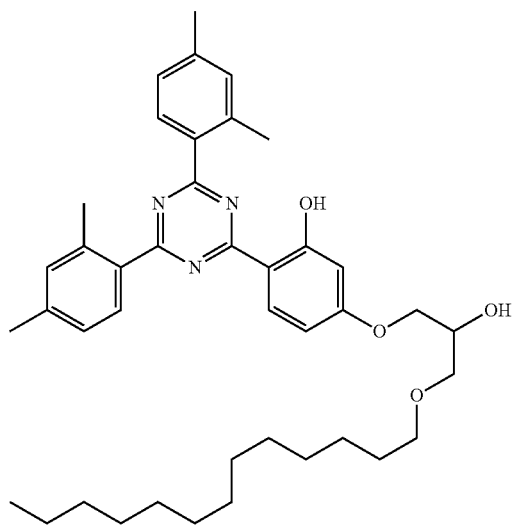
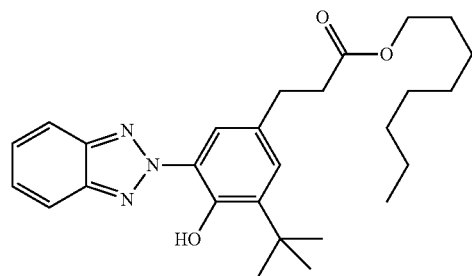


TABLE B-continued







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## Example 2

A liquid crystal mixture containing

CY-3-O4	32.00%	5
CY-5-O2	6.00%	
CCY-3-O2	7.00%	
CCY-1-O2	7.00%	
CCY-3-O3	4.00%	
PYP-2-3	10.00%	10
PYP-2-4	10.00%	
BCH-32	7.00%	
CPGP-5-3	6.00%	
CPGP-5-2	6.00%	
CPGP-1-3	3.00%	
CCP-V-1	2.00%	15
cp. [° C.]:	101.5	
$\Delta n$ [589 nm, 20° C.]:	0.150	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.0	
$K_1$ [20° C.]:	15.1	
$K_3$ [20° C.]:	17.0	
$K_3/K_1$ [20° C.]:	1.13	20
$V_0$ [20° C.]:	2.17 V	

## Example 3

A liquid crystal mixture containing

CY-3-O4	30.00%	30
CY-5-O2	4.00%	
CCY-3-O2	5.00%	
CCY-4-O2	8.00%	
CCY-3-O3	8.00%	
PYP-2-3	10.00%	
PYP-2-4	10.00%	
PGP-2-3	14.00%	35
CPGP-5-3	10.00%	
cp. [° C.]:	98.4	
$\Delta n$ [589 nm, 20° C.]:	0.1631	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.0	
$K_1$ [20° C.]:	15.3	
$K_3$ [20° C.]:	17.2	40
$K_3/K_1$ [20° C.]:	1.12	
$V_0$ [20° C.]:	2.19 V	

## Example 4

A liquid crystal mixture containing

CY-3-O4	19.00%	50
CY-5-O4	18.00%	
CCY-3-O2	6.00%	
CCY-3-O3	6.00%	
CCY-4-O2	6.00%	
CCY-5-O2	6.00%	
CPY-2-O2	9.00%	55
CPY-3-O2	9.00%	
CH-43	3.00%	
CH-45	3.00%	
CCOC-3-3	2.00%	
CCOC-4-3	2.00%	
CCOC-3-5	2.00%	60
CCPC-33	3.00%	
CCPC-34	3.00%	
CPGP-5-3	3.00%	
cp. [° C.]:	113	
$\Delta n$ [589 nm, 20° C.]:	0.1072	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-5.6	65

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## Example 5

A liquid crystal mixture containing

CY-3-O4	26.00%	
CY-3-O2	10.00%	
CCY-3-O2	7.00%	
CCY-3-O3	7.00%	
CCY-4-O2	6.00%	
CCY-5-O2	6.00%	10
CCY-2-1	9.00%	
CCY-3-1	8.00%	
PGP-2-3	10.00%	
CPGP-5-2	3.00%	
CC-3-V1	8.00%	15
cp. [° C.]:	85.9	
$\Delta n$ [589 nm, 20° C.]:	0.1117	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.7	
$K_1$ [20° C.]:	14.7	
$K_3$ [20° C.]:	16.4	
$K_3/K_1$ [20° C.]:	1.11	20
$V_0$ [20° C.]:	1.98 V	

## Example 6

A liquid crystal mixture containing

CY-3-O4	28.00%	30
CCY-3-O2	7.00%	
CCY-3-O3	6.00%	
CCY-4-O2	6.00%	
CCY-5-O2	6.00%	
CCY-3-1	8.00%	
PGP-2-3	13.00%	35
CPGP-5-2	4.00%	
CC-4-V	10.00%	
CK-3-F	4.00%	
CK-4-F	4.00%	
CK-5-F	4.00%	
cp. [° C.]:	85.2	40
$\Delta n$ [589 nm, 20° C.]:	0.1134	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.8	
$K_1$ [20° C.]:	14.3	
$K_3$ [20° C.]:	14.3	
$K_3/K_1$ [20° C.]:	1.00	
$V_0$ [20° C.]:	1.84 V	

## Example 7

A liquid crystal mixture containing

CY-3-O4	28.00%	50
CY-5-O4	15.00%	
CCY-3-O2	8.00%	
CCY-3-O3	8.00%	
CCY-4-O2	8.00%	55
CPGP-5-2	7.00%	
CPGP-5-3	6.00%	
CC-4-V	14.00%	
PGP-2-3	6.00%	60
cp. [° C.]:	83.3	
$\Delta n$ [589 nm, 20° C.]:	0.1107	
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.0	
$K_1$ [20° C.]:	12.6	
$K_3$ [20° C.]:	14.3	
$K_3/K_1$ [20° C.]:	1.14	65
$V_0$ [20° C.]:	2.00 V	

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## Example 8

A liquid crystal mixture containing

CY-3-O4	25.00%
CCY-3-O2	7.00%
CCY-3-O3	7.00%
CCY-4-O2	7.00%
CCY-3-1	7.00%
PGP-2-3	11.00%
CPGP-5-2	8.00%
CC-4-V	16.00%
CK-3-F	4.00%
CK-4-F	4.00%
CK-5-F	4.00%
cp. [° C.]:	87.5
$\Delta n$ [589 nm, 20° C.]:	0.1121
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.0
$K_1$ [20° C.]:	13.1
$K_3$ [20° C.]:	14.5
$K_3/K_1$ [20° C.]:	1.11
$V_0$ [20° C.]:	2.00 V

## Example 9

A liquid crystal mixture containing

CY-3-O4	21.00%
CY-5-O4	13.00%
CCY-3-O2	7.00%
CCY-3-O3	7.00%
CCY-4-O2	6.00%
CPY-3-O2	11.00%
CCY-2-1	7.00%
CCY-3-1	7.00%
PYP-2-3	5.50%
CPGP-5-2	3.50%
CC-3-V1	5.00%
CC-5-V	7.00%
cp. [° C.]:	87.6
$\Delta n$ [589 nm, 20° C.]:	0.1088
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.9
$K_1$ [20° C.]:	15.3
$K_3$ [20° C.]:	16.1
$K_3/K_1$ [20° C.]:	1.05
$V_0$ [20° C.]:	1.93 V

## Example 10

A liquid crystal mixture containing

CY-3-O4	21.00%
CY-5-O4	14.00%
CCY-3-O2	7.00%
CCY-3-O3	6.00%
CCY-4-O2	5.50%
CPY-3-O2	11.00%
CCY-2-1	7.00%
CCY-3-1	7.00%
PYP-2-3	5.00%
CPGP-5-2	4.50%
CC-3-V1	5.50%
CC-5-V	6.50%
cp. [° C.]:	87.5
$\Delta n$ [589 nm, 20° C.]:	0.1092
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.8
$K_1$ [20° C.]:	15.0
$K_3$ [20° C.]:	16.1
$K_3/K_1$ [20° C.]:	1.08
$V_0$ [20° C.]:	1.95 V

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## Example 11

A liquid crystal mixture containing

CY-3-O4	24.50%
CCY-3-O2	8.00%
CCY-3-O3	8.00%
CCY-4-O2	8.00%
CCY-3-1	7.00%
PGP-2-3	10.00%
CPGP-5-2	7.00%
CC-4-V	15.50%
CK-3-F	4.00%
CK-4-F	4.00%
CK-5-F	4.00%
cp. [° C.]:	88.5
$\Delta n$ [589 nm, 20° C.]:	0.1098
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.2
$K_1$ [20° C.]:	13.2
$K_3$ [20° C.]:	14.7
$K_3/K_1$ [20° C.]:	1.11
$V_0$ [20° C.]:	1.97 V

## Example 12

A liquid crystal mixture containing

CY-3-O4	25.00%
CCY-3-O2	7.00%
CCY-3-O3	7.00%
CCY-4-O2	7.00%
CCY-5-O2	4.00%
CCY-3-1	6.00%
PGP-2-3	7.00%
PGP-2-4	3.00%
CPGP-5-2	7.00%
CC-4-V	15.00%
CK-3-F	4.00%
CK-4-F	4.00%
CK-5-F	4.00%
cp. [° C.]:	88.8
$\Delta n$ [589 nm, 20° C.]:	0.1099
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.4
$K_1$ [20° C.]:	14.0
$K_3$ [20° C.]:	14.5
$K_3/K_1$ [20° C.]:	1.04
$V_0$ [20° C.]:	1.94 V

## Example 13

A liquid crystal mixture containing

CY-3-O4	25.00%
CCY-3-O2	7.00%
CCY-3-O3	6.00%
CCY-4-O2	6.00%
CPY-3-O2	12.00%
PGP-2-3	4.00%
CPGP-5-2	6.00%
CCP-V-1	7.00%
CC-4-V	16.00%
CK-3-F	4.00%
CK-4-F	3.00%
CK-5-F	4.00%
cp. [° C.]:	90.4
$\Delta n$ [589 nm, 20° C.]:	0.1090
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.5
$K_1$ [20° C.]:	14.0
$K_3$ [20° C.]:	15.4
$K_3/K_1$ [20° C.]:	1.10
$V_0$ [20° C.]:	1.96 V
$\gamma_1$ [mPa · s, 20°]:	187
LTS Bulk [-30° C.]:	>1000 h

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## Example 14

A liquid crystal mixture containing

CY-3-O4	29.50%
CCY-2-1	10.50%
CCY-3-1	10.00%
CCY-3-O2	6.00%
CCY-4-O2	7.00%
CCY-3-O3	4.00%
PYP-2-3	7.00%
PYP-2-4	6.00%
BCH-32	14.00%
CPGP-5-3	3.00%
CPGP-5-2	3.00%
cp. [° C.]:	100.8
$\Delta n$ [589 nm, 20° C.]:	0.1329
$\Delta \epsilon$ [1 kHz, 20° C.]:	-3.8
$K_1$ [20° C.]:	15.6
$K_3$ [20° C.]:	16.6
$K_3/K_1$ [20° C.]:	1.06
$V_0$ [20° C.]:	2.18 V
LTS Bulk [-20° C.]	>1000 h

## Example 15

A liquid crystal mixture containing

CY-3-O4	32.00%
CY-5-O2	11.00%
CCY-3-O3	10.00%
CCY-5-O2	10.00%
PYP-2-3	8.00%
PYP-2-4	8.00%
BCH-32	2.00%
CPGP-5-3	7.00%
CPGP-5-2	7.00%
CPGP-4-3	5.00%
cp. [° C.]:	100.6
$\Delta n$ [589 nm, 20° C.]:	0.1462
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.4
$K_1$ [20° C.]:	14.7
$K_3$ [20° C.]:	17.3
$K_3/K_1$ [20° C.]:	1.18
$V_0$ [20° C.]:	2.09 V

## Example 16

A liquid crystal mixture containing

CY-3-O4	32.00%
CY-5-O2	7.00%
CCY-2-1	8.00%
CCY-3-O2	8.00%
CCY-4-O2	7.00%
CCY-3-O3	7.00%
PYP-2-3	6.00%
BCH-32	13.00%
CPGP-5-2	6.00%
CPGP-5-3	6.00%
cp. [° C.]:	100.8
$\Delta n$ [589 nm, 20° C.]:	0.1303
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.3
$K_1$ [20° C.]:	15.0
$K_3$ [20° C.]:	17.3
$K_3/K_1$ [20° C.]:	1.15
$V_0$ [20° C.]:	2.12 V
LTS Bulk [-20° C.]	>1000 h

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## Example 17

A liquid crystal mixture containing

CY-3-O4	32.00%
CY-3-O4	29.00%
CY-5-O2	11.00%
CCY-2-1	7.00%
CCY-3-O2	8.00%
CCY-4-O2	7.00%
CCY-3-O3	4.50%
PYP-2-3	6.00%
BCH-32	15.50%
CPGP-5-2	6.00%
CPGP-5-3	6.00%
cp. [° C.]:	100.7
$\Delta n$ [589 nm, 20° C.]:	0.1320
$\Delta \epsilon$ [1 kHz, 20° C.]:	-4.0
$K_1$ [20° C.]:	16.1
$K_3$ [20° C.]:	17.3
$K_3/K_1$ [20° C.]:	1.07
$V_0$ [20° C.]:	2.16 V
LTS Bulk [-20° C.]	>1000 h

## Example 18

A liquid crystal mixture containing

CY-3-O4	32.00%
CY-5-O2	6.00%
CCY-2-1	8.00%
CCY-3-1	3.00%
CCY-3-O2	7.00%
CCY-4-O2	7.00%
CCY-3-O3	5.00%
PYP-2-3	8.00%
BCH-32	10.00%
CPGP-5-2	6.00%
CPGP-5-3	6.00%
CPGP-4-3	2.00%
cp. [° C.]:	104.7
$\Delta n$ [589 nm, 20° C.]:	0.1360
$K_1$ [20° C.]:	16.7
$K_3$ [20° C.]:	17.7
$K_3/K_1$ [20° C.]:	1.06
$V_0$ [20° C.]:	2.25 V
LTS Bulk [-20° C.]	>1000 h

## Example 19

A liquid crystal mixture containing

CY-3-O4	29.00%
CCY-2-1	10.00%
CCY-3-1	10.00%
CCY-3-O2	7.00%
CCY-4-O2	7.00%
CCY-3-O3	6.00%
PYP-2-3	8.00%
PYP-2-4	5.00%
BCH-32	11.00%
CPGP-5-3	3.00%
CPGP-5-2	3.00%
CPGP-4-3	1.00%
cp. [° C.]:	103.8
$\Delta n$ [589 nm, 20° C.]:	0.1331
$K_1$ [20° C.]:	16.7
$K_3$ [20° C.]:	17.2
$K_3/K_1$ [20° C.]:	1.03
$V_0$ [20° C.]:	2.16 V
LTS Bulk [-20° C.]	>1000 h

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### Example 20

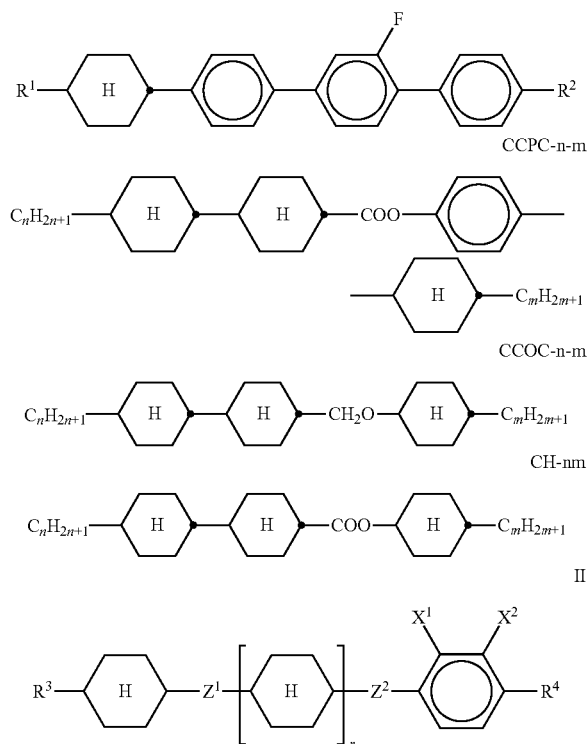
A liquid crystal mixture containing

CY-3-O2	7.00%
CY-3-O4	11.00%
CCY-3-O2	3.00%
CCY-3-O3	7.00%
CCY-4-O2	8.00%
CPY-2-O2	8.00%
CPY-3-O2	8.00%
CC-3-V	20.50%
CC-5-V	7.00%
CC-3-V1	6.00%
CPGP-5-2	1.50%
PYP-2-3	9.00%
PYP-2-4	4.00%
cp. [° C.]:	84.5
Δn [589 nm, 20° C.]:	0.1107

The entire disclosures of all applications, patents and publications, cited herein and of corresponding U.S. application Ser. No. 12/601,567, filed Nov. 24, 2009 are incorporated by reference herein.

The invention claimed is:

1. A liquid crystalline medium containing  
at least one compound of formula I, and  
at least one compound of formula CCPC-n-m, CCOC-n-m  
and CH-nm, and  
at least one compound of formula II



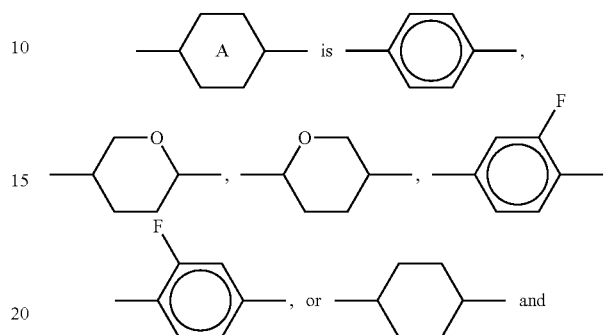
wherein

R<sup>1</sup> to R<sup>2</sup> are each independently alkyl or alkoxy with 1 to 8 C atoms, wherein one or more CH<sub>2</sub>-groups are optionally replaced by —CH=CH—, —CF<sub>2</sub>O or —O— in a way that —O— atoms are not linked directly to one another, and

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n and m are each independently 1 to 6,

R<sup>3</sup> to R<sup>4</sup> are each independently alkyl or alkoxy with 1 to 8 C atoms, wherein one or more CH<sub>2</sub>-groups are optionally replaced by —CH=CH—, —CF<sub>2</sub>O or —O— in a way that —O— atoms are not linked directly to one another.

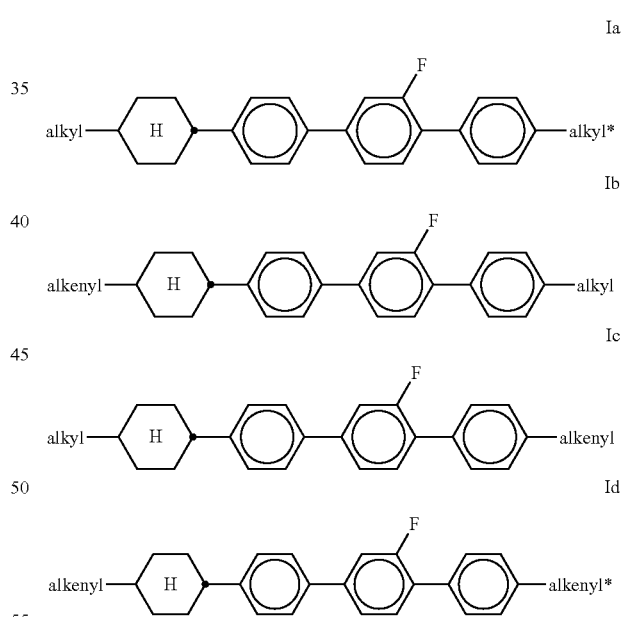


$X^1$  and  $X^2$  are each independently F, Cl or  $CF_3$ ,

$Z^1$  and  $Z^2$  are each independently a single bond,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{O}-$ ,  $-\text{OCH}_2-$ ,  $-\text{CF}_2\text{O}-$ ,  $-\text{OCF}_2-$ , or  $-\text{COO}-$ , and

$r$  is 0 or 1.

2. A liquid crystalline medium according to claim 1, comprising one or more compounds of the following formulae

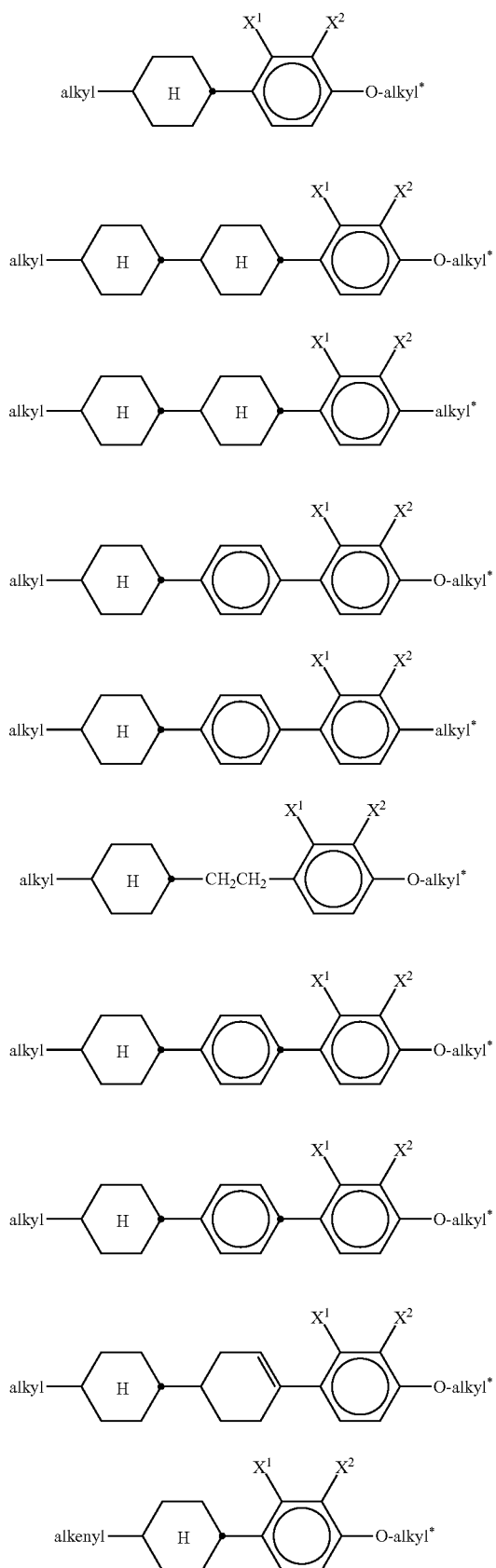


wherein

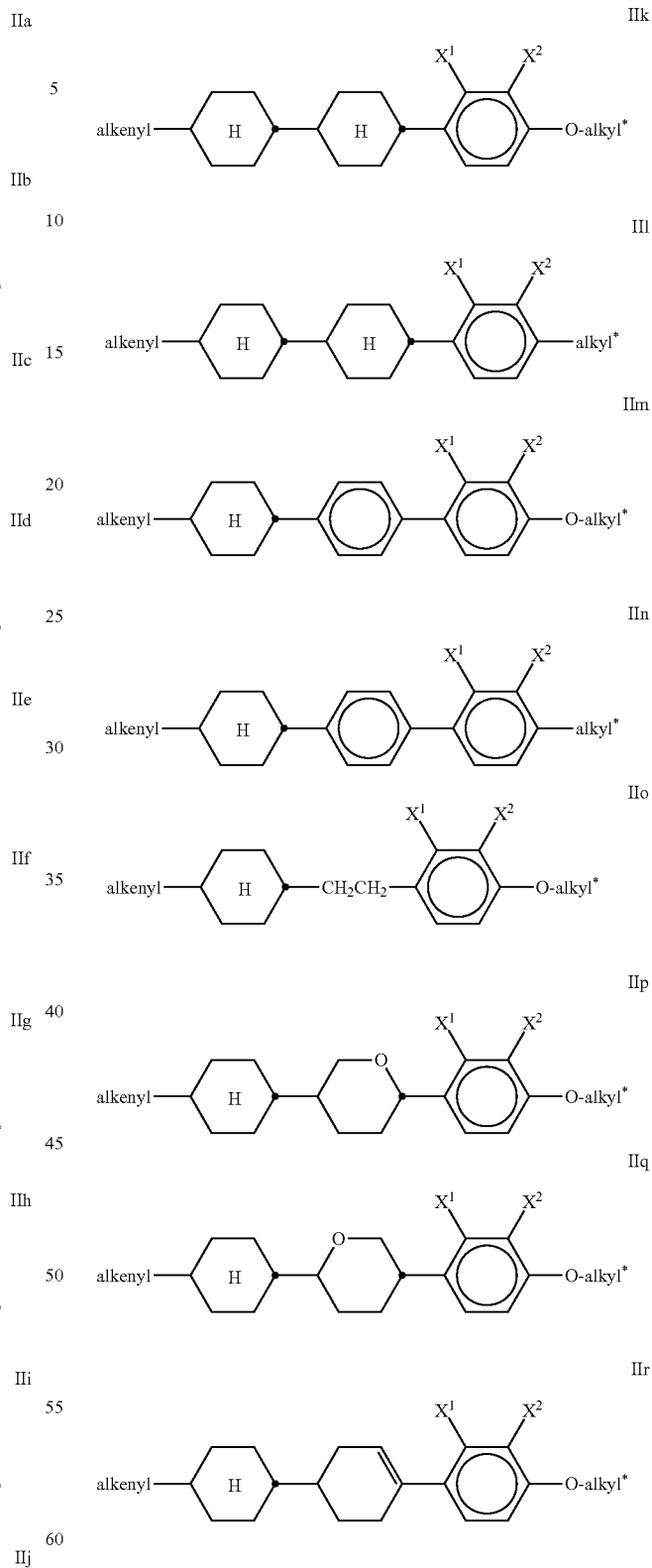
alkyl and alkyl\* independently of each other denote C<sub>1-6</sub>-alkyl and

alkenyl and alkenyl\* independently of each other denote C<sub>2-6</sub>-alkenyl.

3. A liquid crystalline medium according to claim 2, comprising one or more compounds of formula Ia.
4. A liquid crystalline medium according to claim 1, comprising one or more compounds of the following formulae IIa to IIr.

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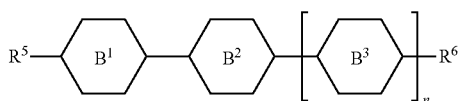


wherein

alkyl and alkyl\* independently of each other denote C<sub>1-6</sub>-alkyl,alkenyl denotes C<sub>2-6</sub>-alkenyl, andX<sup>1</sup> and X<sup>2</sup> are each independently F, Cl or CF<sub>3</sub>.

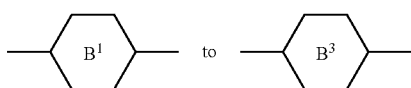
57

5. A liquid crystalline medium according to claim 1, further comprising one or more compounds of formula III

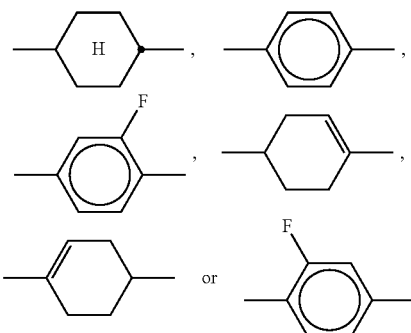


wherein

R<sup>5</sup> and R<sup>6</sup> are independently of each other alkyl or alkoxy with 1 to 8 C atoms, wherein one or more CH<sub>2</sub>-groups are optionally replaced by —CH=CH—,



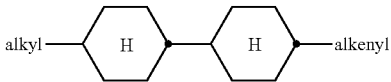
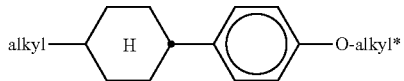
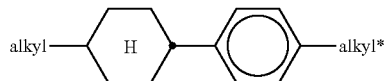
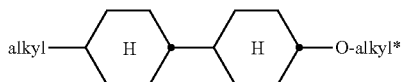
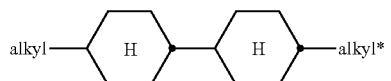
are independently of each other



and

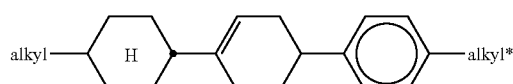
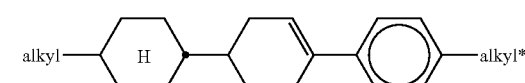
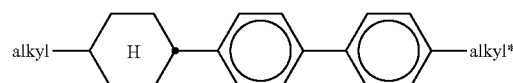
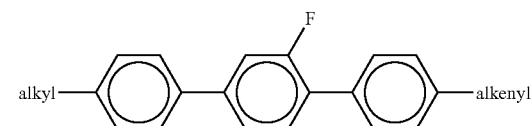
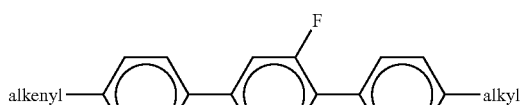
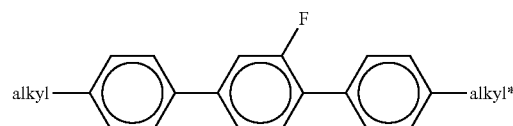
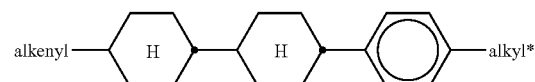
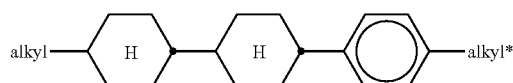
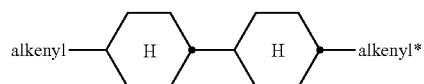
n is 0 or 1.

6. A liquid crystalline medium according to claim 5, comprising one or more compounds of formulae IIIa to IIIn



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wherein

alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, and

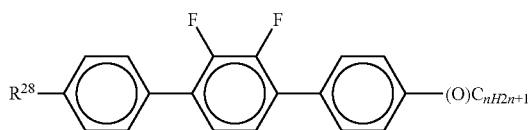
alkenyl and alkenyl\* each, independently of one another, denote a straight-chain alkenyl radical having 2-6 C atoms.

7. A liquid crystalline medium according to claim 5, wherein the proportion of the compound of formula III in the liquid crystalline medium as a whole is 3 to 50% by weight.

8. A liquid crystalline medium according to claim 1, wherein the proportion of the compounds of formula I in the liquid crystalline medium as a whole is 1 to 30% by weight.

9. A liquid crystalline medium according to claim 1, further comprising a compound of Z-15

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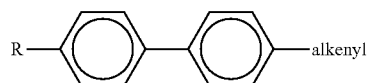
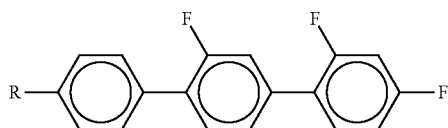


wherein

$R^{28}$  is alkyl or alkoxy with 1 to 8 C atoms, wherein one or more  $CH_2$ -groups are optionally replaced by  $-CH=CH-$ ,  $-CF_2O$  or  $-O-$  in a way that  $-O-$  atoms are not linked directly to one another, and

$n$  is 1 to 6.

**10.** A liquid crystalline medium according to claim 1, further comprising one or more biphenyl or terphenyl compounds of formula T-1 and/or B-1

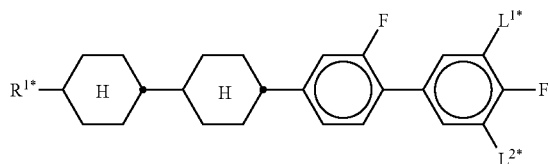
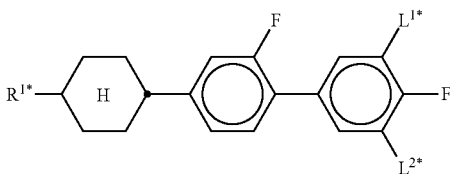
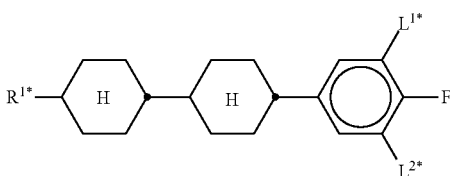


in which

$R$  denotes alkyl, alkenyl, alkoxy, alkylalkoxy or alkenylalkoxy having 1 or 2 to 6 C atoms, and

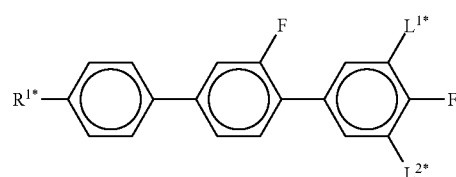
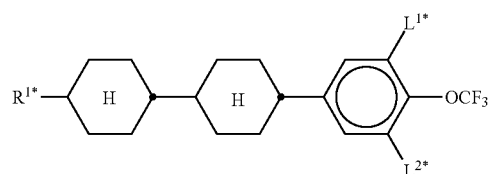
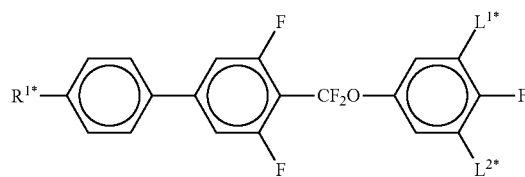
alkenyl denotes a straight-chain alkenyl radical having 2-6 C atoms.

**11.** A liquid crystalline medium according to claim 1, further comprising one or more compounds of formula P-1 to P-6



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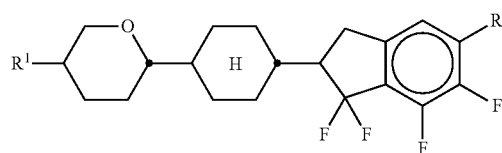
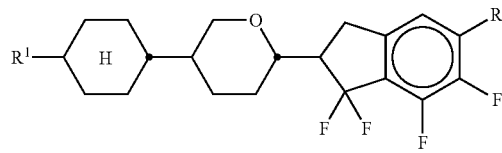
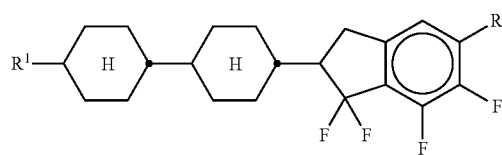
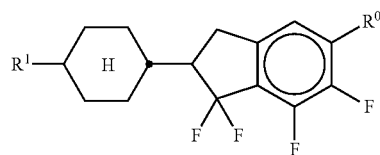


in which

$R^{1*}$  is alkyl or alkoxy with 1 to 8 C atoms, wherein one or more  $CH_2$ -groups are optionally replaced by  $-CH=CH-$ ,  $-CF_2O$  or  $-O-$  in a way that  $-O-$  atoms are not linked directly to one another, and

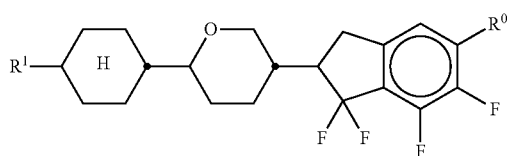
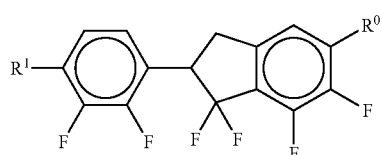
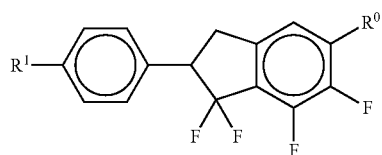
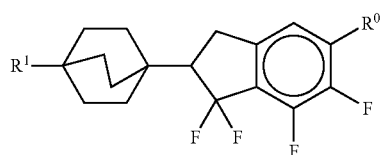
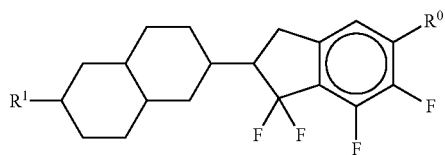
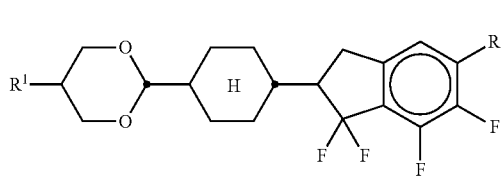
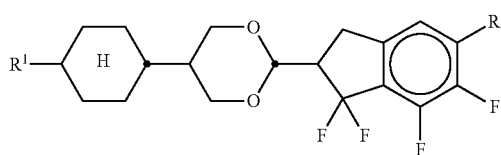
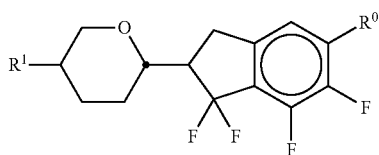
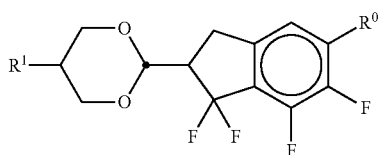
$L^{1*}$  and  $L^{2*}$  each independently of one another denote H or F.

**12.** A liquid crystalline medium according to claim 1, further comprising one or more indane compounds of formulae In-1 to In-18

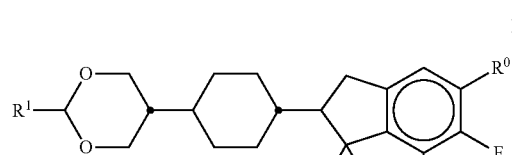
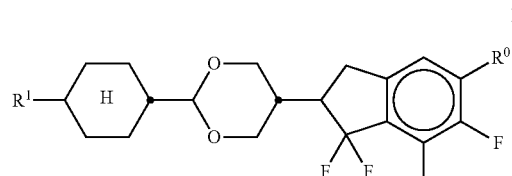
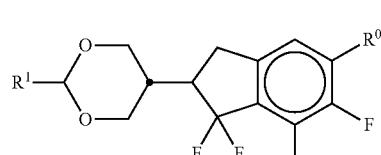
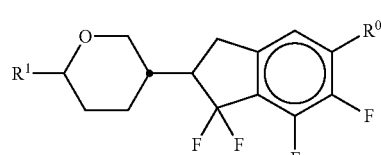
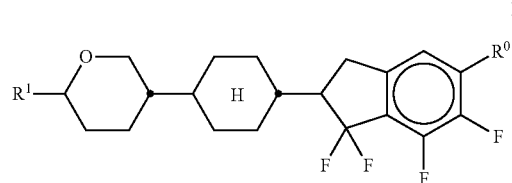


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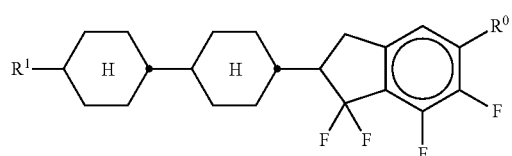
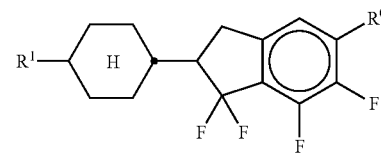
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wherein

$R^1$  and  $R^0$  are each independently alkyl or alkoxy with 1 to 8 C atoms, wherein one or more  $CH_2$ -groups are optionally replaced by  $-CH=CH-$ ,  $-CF_2O$  or  $-O-$  in a way that  $-O-$  atoms are not linked directly to one another.

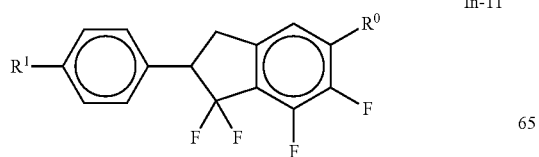
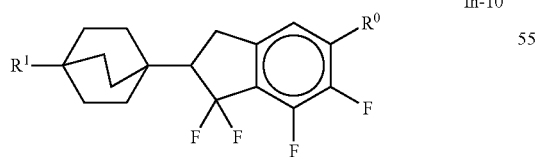
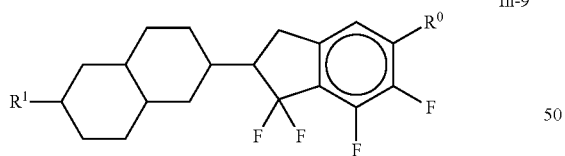
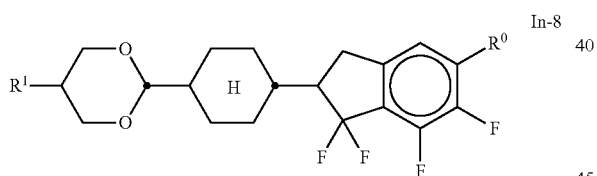
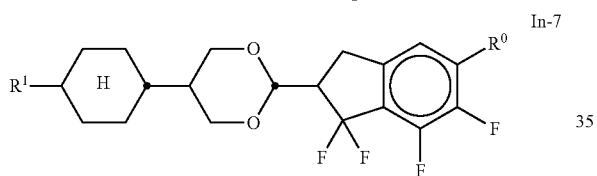
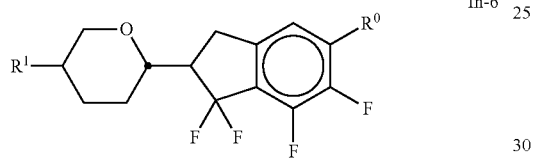
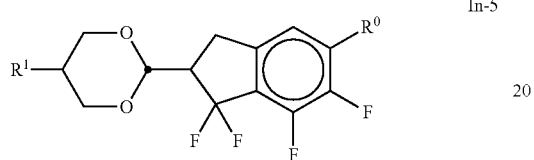
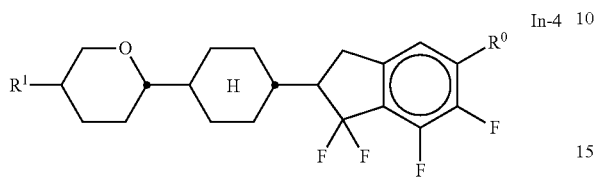
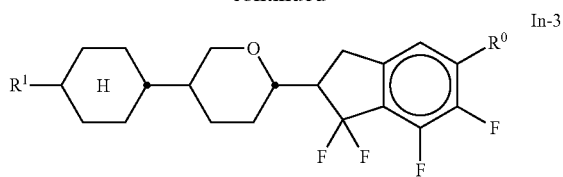
**13.** A liquid crystalline medium according to claim 1, further comprising one or more indane compounds of formulae In-1 to In-18



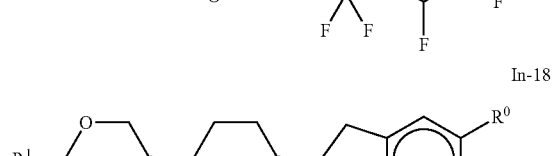
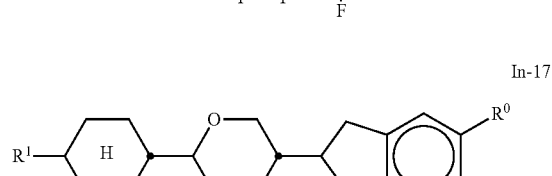
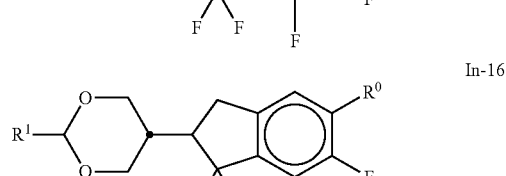
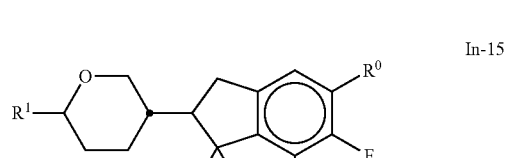
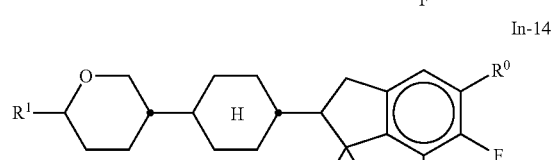
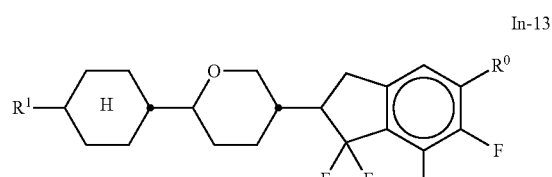
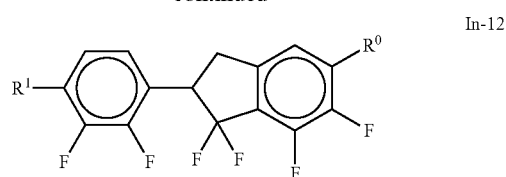


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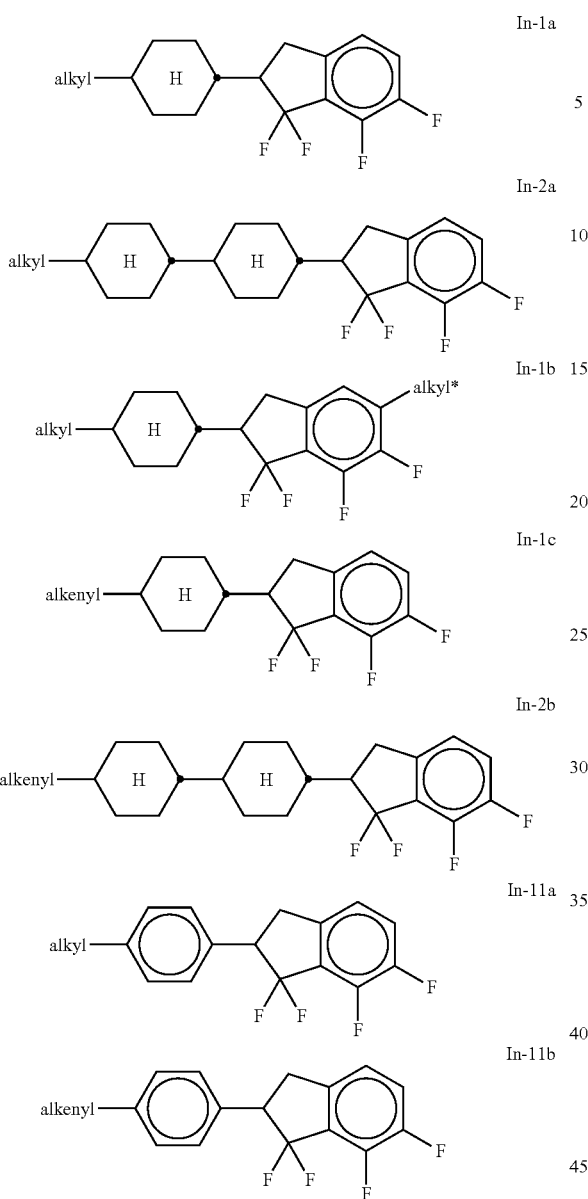
wherein

R<sup>1</sup> denotes a straight-chain alkyl radical having 1-6 C atoms or a straight-chain alkenyl radical having 2-6 C atoms, and

R<sup>0</sup> denotes H or a straight-chain alkyl radical having 1-6 C atoms.

14. A liquid crystalline medium according to claim 1, further comprising one or more indane compounds of the following formulae

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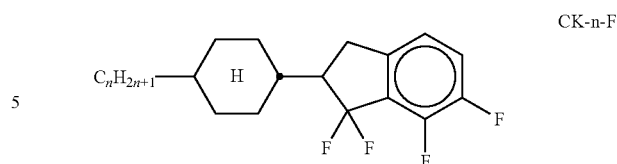
wherein

alkyl and alkyl\* each, independently of one another, denote a straight-chain alkyl radical having 1-6 C atoms, and  
alkenyl denotes a straight-chain alkenyl radical having 2-6 C atoms.

15. A liquid crystalline medium according to claim 1, further comprising one or more UV absorbers, nanoparticles, nanobeads, microparticles, antioxidants and/or free-radical scavengers.

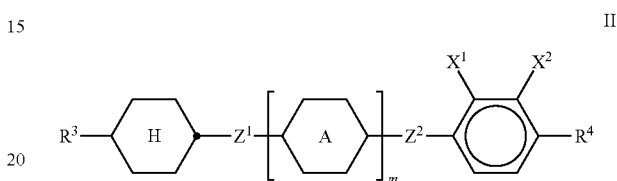
16. A liquid crystalline medium according to claim 1, further comprising a compound of formula CK-n-F

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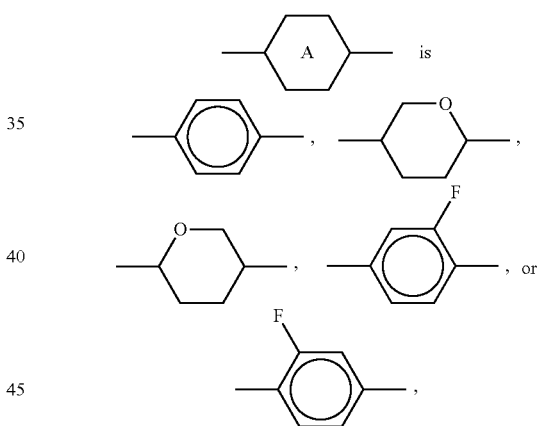
in which n is 1-6.

17. A liquid crystalline medium according to claim 1, comprising a compound of formula II,



wherein

$R^3$  to  $R^4$  are each independently alkyl or alkoxy with 1 to 8 C atoms, wherein one or more  $CH_2$ -groups are optionally replaced by  $-CH=CH-$ ,  $-CF_2O-$  or  $-O-$  in a way that  $-O-$  atoms are not linked directly to one another,



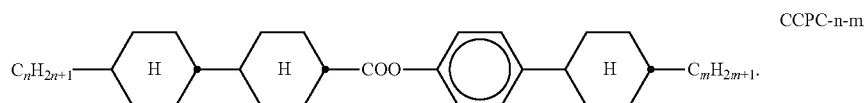
$X^1$  and  $X^2$  are each independently F, Cl or  $CF_3$ ,

$Z^1$  and  $Z^2$  are each independently a single bond,  $-CH_2CH_2-$ ,  $-CH_2O-$ ,  $-OCH_2-$ ,  $-CF_2O-$ ,  $-OCF_2-$ , or  $-COO-$ , and

r is 0 or 1.

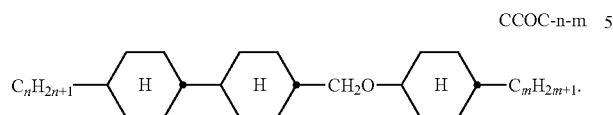
18. A liquid crystalline medium according to claim 1, wherein the proportion of the compound of formula II in the liquid crystalline medium as a whole is at least 30% by weight.

19. A liquid crystalline medium according to claim 1, which comprises a compound of formula CCPC-n-m

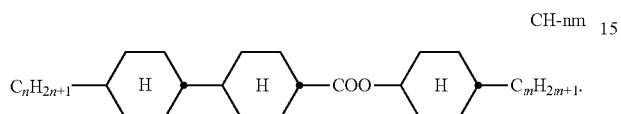


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20. A liquid crystalline medium according to claim 1,  
which comprises a compound of formula CCOC-n-m



21. A liquid crystalline medium according to claim 1,  
which comprises a compound of formula CH-nm <sup>10</sup>



22. A method for achieving an electrooptical effect, comprising addressing a liquid crystalline medium according to claim 1. <sup>20</sup>

23. An electrooptical liquid crystal display containing a liquid crystalline medium according to claim 1.

24. An electrooptical display according to claim 23, which has active matrix addressing and is based on the ECB, VA, ASV, PS-VA, MVA, FFS or PALC mode. <sup>25</sup>

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